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② LEVEL II

SUPERHARD TRANSPARENT COATINGS

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Fort Eustis, Va. 23604

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APPLIED TECHNOLOGY LABORATORY POSITION STATEMENT

This report was prepared by the Goodyear Aerospace Corporation, Arizona Division, under the terms of Contract DAAJ02-76-C-0004.

The objectives of this contractual effort were: (1) to evaluate the feasibility and practicality of producing and applying superhard transparent coatings to a full-scale helicopter windshield, and (2) to subsequently provide windshields for a limited field-service evaluation. This report presents the results of the first objective. Results of the limited field-service evaluation will be published upon completion.

The findings and results of this report offer a highly promising approach to improving the reliability and maintainability of plastic Army helicopter transparencies by improving their resistance to in-service abrasion and scratching, thus reducing the time and expense involved in the replacement of these transparencies. A major benefit of this program, if successful, will be the ability to use windshield wipers in conjunction with plastic transparencies, thereby taking advantage of their lower weight compared to glass transparencies and enhancing the overall performance and utility of the aircraft. Finally, improvements in the performance of these transparencies will result in reduced life-cycle costs for Army helicopter transparencies.

The next phase of this effort is to conduct a 6-month Army field-service evaluation of 10 UH-1 helicopter windshields coated with the recommended coating (No. 210) from this effort.

The technical monitor for this contract was Thomas E. Condon of the Military Operations Technology Division of this Laboratory.

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Army helicopter glazings have been particularly susceptible to windshield damage from wiper abrasion and dust clouds generated by the rotor vortex, as evidenced by Army operational service experience. The short life expectancy of acrylic windows required frequent and expensive replacement. The purpose of this program was to evaluate transparent hard coatings

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20. Abstract (cont)

which would extend the service life of new glazings, and possibly, through resurfacing, some panels already in service.

The first requirement was to choose, through a series of tests, the better of several formulations developed by the Marks Polarized Corporation. The coating chosen was then to be field tested on full-scale helicopter glazings. Problems with the formulations resulted in unsuccessful attempts at modification and ultimately, the development of new formulations which are now ready for field testing.

This final report concerns theoretical chemistry, the problems encountered in developing a serviceable coating, the laboratory test results of both old and new formulations and recommendations for full-scale processing. Appendixes to this report contain test methods and equipment used in the testing sequences which are not found in standard procedures.

PREFACE

This final report concerns the verification of the coating formulations and processing developed by the Marks Polarized Corporation and the subsequent development and testing by Goodyear Aerospace Corporation of new variations on polysilicic acid based hard coatings.

The program was performed by Goodyear Aerospace Corporation, Arizona Division, Litchfield Park, Arizona, under Contract Number DAAJ02-76-C-0004.

The work was done for the Applied Technology Laboratory, U. S. Army Research and Technology Laboratories (AVRADCOM), Fort Eustis, Virginia. The Project Engineer was Mr. Thomas E. Condon.

Mr. G. E. Wintermute was the Project Engineer for Goodyear Aerospace.

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SECTION I

INTRODUCTION

This report concerns the development and testing of candidate coatings formulated toward solving the Army's problem of frequent glazing replacement. Most hard coatings marketed have utilized silicic acid chemistry as a source of submicron silica. These are no exceptions. The formulations contain a binder, a filler, a cross-linker, and solvents. If the silica from the silicic acid is considered a hard filler, the particle content will depend upon a balanced formulation which also has the attributes of flow and adhesion as well as ultraviolet and hydrolytic stability. Further hardening to a "superhardness" may be accomplished by inserting a small quantity of submicron aluminum oxide or silicon dioxide powders into the formulation, but not without problems. The development process and testing are detailed along with the chemistry of the coatings.

Task I will be discussed with reference to materials, processing and procurement cited in report USAAMRDL-TR-75-22,[1] with specific attention to four variations of the basic system which were applied to three substrates, both primed and unprimed.

Task II refers to screening the previous formulations by testing for adhesion, hardness, and appearance after being subjected to a 120° F, 95-percent relative humidity environment until failure. Modifications of these mixes were attempted to obtain better properties. A change in primer constituents was also considered. None of these measures resulted in complete success.

Because no single airworthy coating was developed in the previous tasks, Task III was altered from field testing to the development of new coating, also based on a polysilicic acid system, which theoretically would exhibit better adhesion, hardness, and appearance.

Processing and equipment are discussed last in preparation for eventual full-scale field testing.

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[1] A. Marks, Superhard Transparent Coatings, USAAMRDL-TR-75-22, Eustis Directorate, U.S. Army Air Mobility Research and Development Laboratory, Fort Eustis, Virginia 23604, April 1975, AD A010388.

SECTION II

COATING FORMULATION, MARKS CONCEPT

1. GENERAL

The purpose of Task I was to verify the superhard coating compositions recommended by USAAMRDL-TR-75-22 and to substantiate the producibility and applicability of the candidate coatings.

This section concerns the production and application of Marks' coating formulations 119, 120, 129C, and 130, as well as primer formulations FA5 and FA6.

The Goodyear Aerospace coating formulations of the Marks concept have not changed with respect to the solids mix ratio from the formulations documented in USAAMRDL-TR-75-22. Compounding methods and solvent additions have been altered to achieve improved compatibility between coating components and to improve the resulting coating film.

2. PREPARATION OF BASIC COATING MIXTURES

a. General

Three basic mixtures were required for formulating the superhard coatings. The processing of these mixtures is discussed in the following paragraphs.

b. Polyvinyl Alcohol Solution

Polyvinyl alcohol (PVA) is a water soluble synthetic resin which is dissolved in hot water. The resulting solution should be clear and have a solids content of 10 percent. Upon standing for several days the solution will become cloudy, at which time it should be remelted or discarded.

c. Polysilicic Acid Mixture

The polysilicic acid mixture is prepared by reacting 85 parts by weight of tetraethyl orthosilicate with 15 parts by weight of water. The reaction is catalyzed by the addition of concentrated hydrochloric acid (1 percent based on the amount of water required). The tetraethyl orthosilicate-water-hydrochloric acid solution requires vigorous agitation to complete the reaction. The resulting mixture is clear and consists of polysilicic acid and

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ethanol. The solids content of this mixture, based on SiO_2, is 24.6 percent. The polysilicic acid solution is further diluted to 18.3 percent using water. This dilution is accomplished just prior to its incorporation into the coating mixture.

The polysilicic acid solution will convert to a suspension of silica crystallites upon the application of heat. This formation of submicron silica particles occurs during the curing process of the coating. The chemistry follows.

Tetraethyl orthosilicate is synthesized from silicon tetrachloride and anhydrous ethyl alcohol.

$$SiCl_4 + 4\ C_2H_5OH \longrightarrow Si(OC_2H_5)_4 + 4\ HCl \uparrow$$
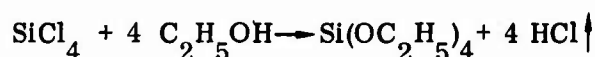
Complete hydrolysis of ethyl silicate will theoretically produce silica and ethyl alcohol. The reaction for 100-percent hydrolysis is

$$Si(OC_2H_5)_4 + 2H_2O \xrightarrow{H^+ \text{ or } OH^-} SiO_2 + 4C_2H_5OH \ .$$
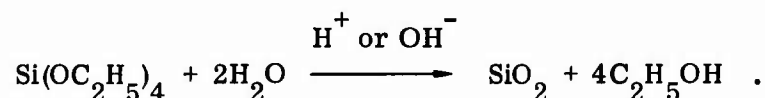
(A variation in this theory is discussed later in the text.)

The Marks report (USAAMRDL-TR-75-22) recommends the removal of a portion of the ethanol to improve the compatibility between the polysilicic acid mixture and PVA solution. Attempts were made to remove a portion of the ethanol through vacuum distillation. The process was found to be time consuming and ultimately unneeded and was therefore discontinued.

d. Alumina-Water Suspension

The fumed aluminum oxide (Alon)⊛ particles must be dispersed in water. To achieve this dispersion, a 10-percent mixture of Alon and water was circulated through a Gaulin Model 15M Sub-Micron Disperser at 9500 psi. Theoretically, the Alon-water mixture was circulated through the disperser 10 times to completely shear the glomerates.

The Alon-water suspension consists of a fairly wide range of submicron particle sizes, of which only the smaller particles will result in a clear

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⊛ Alon - trademark of Cabot Corporation, Boston, MA.

coating. To separate the Alon particles, a Sorvall high-speed centrifuge was utilized. The heavier opaque particles were precipitated and removed at the lower rpm. A translucent gel which was incorporated into the 119, 120, and 130 superhard coatings was precipitated at between 10,000 and 15,000 rpm. The solids content of this gel was approximately 45 percent.

3. PREPARATION OF COATING COMPOSITES

a. General

The coatings in general are formulated to the specific method of application utilized. A typical spin coating formulation will use a minimum amount of additional water or solvents, whereas a typical flow coating formulation will require additional water or solvent to produce a smooth, clear film approximately 10 microns thick. The solids ratios of the superhard coatings, as illustrated in Table 1, remain the same regardless of the method of coating application. Table 2 documents the coating formulations recommended by Marks. These formulations are all designed for spin coating applications. Table 3 illustrates the coating formulations modified by Goodyear Aerospace.

b. Code 129C and Modified 129C Coatings

The 129C coating formulation is prepared by first adding the required amount of water to the polysilicic acid solution. This is accomplished prior to the addition of the PVA to assure compatibility between the PVA and poly-silicic acid. The PVA solution is then added to the polysilicic acid. This step requires the aid of a mechanical mixer. The resulting coating solution should be clear.

The modified 129C coating is compounded in the same manner as the 129C except that the PVA solution contains approximately 2 percent DAA.

c. Code 119 and 130 Coatings

The 119 and 130 coatings are compounded similar to the 129C coating except that the addition of the Alon-water gel follows that of the PVA. The resulting coating solution will have a milky appearance caused by the addition of the Alon-water gel.

TABLE 1. SOLIDS COMPOSITION OF SUPERHARD COATINGS

Coating number code	Percent solids by weight		
	Alon	Silica	Polyvinyl alcohol
119	20	75	5
120	22	78	0
129C	0	70	30
129C modified	0	70	30
130	15	70	15

TABLE 2. MARKS SUPERHARD COATINGS FORMULATIONS

	Percent solids	119	120	129C	130
Polysilicic acid	18.3	80.9	89.3	55.9	67.3
PVA	10	9.8	-	44.1	26.5
Alon-water gel	43	9.3	10.7	-	6.2

TABLE 3. MODIFICATIONS TO MARKS' SUPERHARD COATINGS FORMULATIONS

	Percent solids	129C		129C Modified	119	120	130
		Flow	Spin				
Polysilicic acid	18.3	56 pbw	56 pbw	56 pbw	80.9 pbw	89.3 pbw	67.3 pbw
PVA	10	44	44	-	9.8	-	26.5
PVA/DAA*	10	-	-	44	-	-	-
Alon/water gel	45	-	-	-	9.3	10.7	6.2
Water (added)	-	69	17	69	97	109	83

*PVA/DAA ratio is 25/5.

NOTES:

1. DAA – Diacetone acrylamide.

2. PVA – Elvanol 71-30.

3. All coatings unless otherwise specified are formulated for flow coating applications.

4. Pbw – parts by weight.

d. Code 120 Coating

The 120 coating is compounded in the same manner as the 119 and 130 coatings except that no PVA component is utilized. The resulting 120 coating solution also will be milky in appearance.

4. REQUIRED PRIMERS

a. General

The use of primers is required to effect adhesion between the superhard coatings and plastic substrates. Table 4 documents the primer formulations. The formulation will depend upon the specific method of application and type of plastic substrate being utilized.

No primers are required when the superhard coatings are applied to glass substrates.

b. Preparation and Cure of Primers

The primers are prepared by combining the required components shown in Table 4 and heating the mixture to 140 to 160° F, thereby forming a clear solution.

The primer is applied to the plastic substrate, is allowed to air dry, and is then oven dried for 2 hours at 190° F.

TABLE 4. PRIMER FORMULATIONS

	Spin coating formulations		Flow coating formulations	
	FA5 (acrylic)	FA6 (polycarbonate)	FA5 (acrylic)	FA6 (polycarbonate)
Formvar 7/95E	5 pbw	5 pbw	1 pbw	1.25 pbw
Acetic acid	95	92	99	98
DAA	-	3	-	0.75

Pbw = parts by weight.

SECTION III

COATINGS VERIFICATION, MARKS CONCEPT

1. VERIFICATION OF APPLIED COATINGS

    a. General

    This section concerns the verification of the coatings reported in the previous section and is a continuation of Task I. Table A-1 in Appendix A is a Goodyear Aerospace-applied superhard coating panel identification log indicating coating formulation, method of coating application, adhesion, hardness, and general coating appearance. Table A-2 is the same type of log documenting the as-received properties of the two Marks-applied coatings.

    The verification that Goodyear Aerospace's reproduction of Marks' superhard coatings was successfully accomplished is based on the comparisons given in the following paragraphs.

    b. Coating Formulations

    Goodyear Aerospace superhard coating solutions utilize the same solids ratio as documented in USAAMRDL-TR-75-22.

    c. Hardness

    Goodyear Aerospace applied superhard coatings were consistently harder than the same formulations applied by Marks. The hardness evaluation was conducted using 00 steel wool. The successful resistance to 00 steel wool represents a minimum Mohs' hardness of 5.5.

    Tables A-1 and A-2 illustrate the comparison in hardness between the Goodyear Aerospace and Marks applied coatings as represented by the abrasion-resistant column. Nearly all of the Goodyear Aerospace applied coatings were resistant to the steel wool abrasion test, while the coating hardness of the panels submitted by Marks was somewhat softer than a Mohs' hardness of 5.5.

    d. Abrasion Resistance

    Mechanical abrasion resistance tests were performed on both Goodyear Aerospace and Marks test panels using the reciprocating arm abrader and

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the salt blast abrasion test device. Comparison data are shown in Tables
A-3 and A-4. Results documented in these tables illustrate the excellent
abrasion resistance of the Goodyear Aerospace applied 129C and modified
129C coatings.

e. Appearance

The appearance of the Goodyear Aerospace and Marks applied coatings was
of similar quality. Both coatings contained a small amount of particle in-
clusions in the cured film. It has not been determined if these particles
form during the film drying process or are present in the coating solution.
Attempts to eliminate the particles by filtering the coating solution were not
successful.

2. SUMMARY OF TASK I

Task I, which concerned verification of the coating formulations, has been com-
pleted. Fundamental modifications were made to improve viscosity and to reduce
film shrinkage. Flow and spin coating techniques were used on flat panels. Both
primers were of a predominantly glacial acetic acid content. Film fracturing
appeared in all formulations containing the Alon filler. Films without the filler
appeared to be less fracture prone, but more sensitive to humidity conditions.
Hardness and abrasion resistance remained as distinct advantages.

SECTION IV

EVALUATION AND SELECTION OF COATING

1. **GENERAL**

The purpose of Task II was to evaluate the four verified coatings from the previous sections by a series of tests which would identify one coating with the best combination of physical properties. Coatings for the tests were to be applied to stretched and unstretched acrylic substrates and polycarbonate. This section concerns the work involved in making the choice. Data from Task I (Tables A-5 and A-6 in Appendix A) indicated that the coatings were highly susceptible to humidity conditions. As a consequence, tests requiring environmental exposure were first used as a screening measure.

2. **ENVIRONMENTAL TESTING**

   a. **Test Plan**

   The test plan was approved and is outlined in Section IX of this report. Specimens (1 ft × 1 ft × 1/8 in.) of stretched Plex 55, as-cast Plex II, and polycarbonate were cleaned in preparation for priming, coating, and testing according to the test plan. Basically, the four Marks' coatings were formulated and coated onto stretched Plex 55 substrates. The original formulations were modified slightly by the addition of more water for better processing characteristics, but were not changed in any other manner. The FA5 primer was used in all instances. Primers and coatings were all processed with identical room temperatures and oven cures. All the coatings exhibited excellent qualities of hardness, adhesion, abrasion resistance, light transmission, and minimum haze.

   b. **Screening Procedure**

   The four coatings, No. 119, No. 120, No. 129C, and No. 130M, were screened by subjection to natural outdoor weathering, 95-percent relative humidity at +120 deg F, and ultraviolet (UV) radiation. These tests were chosen as being the more severe for any transparent plastic composite. Of the four coatings, most retained their rating above 5.5 on the Mohs' scale of hardness for the duration of the tests. The severest test was that of the humidity exposure which represented a tropical condition.

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c. Screening Test Results

The results of the testing are shown in Table 5.

By placing the coatings in order of polyvinyl alcohol (PVA) content, as shown in Table 6, it appeared that the ability of the formulation to withstand the humidity exposure was contingent upon the amount of PVA being between 5 and 15 parts by weight. The 120 coating had no PVA content. A photograph of the coated specimens is shown in Figure 1.

d. Discussion of Results and Coating Selection

The 129C failure consisted of massive small broken bubbles approximately 1/8 in. apart. The 130M may have been starting a similar failure mode except that cloudy spots appeared which were slightly larger and farther apart. The 120 coating exhibited an adhesive failure using the tape test of CLA-12799A, procedures "A" and "B", but did not spot. The 119 held up very well. Figure 2 shows the No. 119 coating on the control specimen and a specimen subjected to 1344 hours exposure of 120° F at 95 percent relative humidity. The light transmission and haze measurements of the control and test specimens were:

	Light Transmission (percent)	Haze (percent)
Control	92.4	1.0
Test Specimen	88.0	5.2

A fifth coating, 129 C/M, also failed in less than 7 hours. The formulation was the same as the 129C except for the addition of diacetone acrylamide (DAA) in a 25/5 ratio of PVA to DAA. The coating blistered in a pattern similar to the 130M coating and also exhibited a haze and metallic iridescence.

The relative success of the 119 coating determined that it should be the formulation scheduled for further testing in the Task II program.

e. Full-Scale Coating of UH-1 Windshield

During the processing of the 119 formulation and the other coatings on over 50 panels, microcracking of the coating was sometimes noted after curing or, if not then, after weathering or UV exposure. As a check, a full-scale UH-1

TABLE 5. HUMIDITY EXPOSURE STATUS

Test	95 percent relative humidity at 120° F	UV exposure	Natural weathering	Remarks
Coating				
119	No failure after 39 days	No failure after 54 days	No failure after 55 days	Coating initially microcracked
120	Failed after 17 days	No failure after 54 days	No failure after 55 days	Adhesion failure
129C	Failed after less than 7 hours	No failure after 54 days	No failure after 55 days	Blistered
130M	Failed after less than 18 hours	No failure after 18 days	No failure after 19 days	Spotted

TABLE 6. PERCENT SOLIDS BY WEIGHT

Coating	Alon	Silica	PVA	Time to failure
129C	0	70	30	Less than 7 hours
130M	15	70	15	Less than 18 hours
119	20	75	5	54 days (no change)
120	22	78	0	17 days
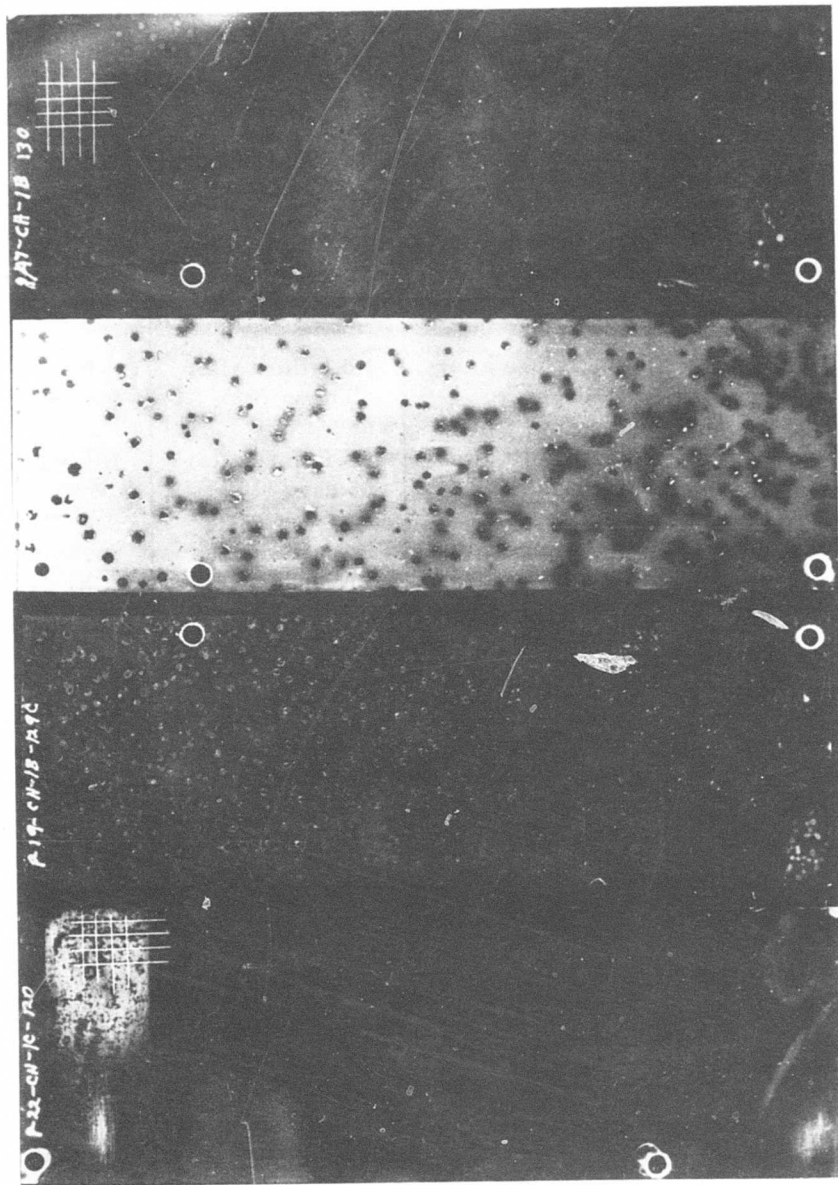
NO. 120
ADHESION FAILURE
17 DAYS

NO. 129C
COATING FAILURE
<7 HOURS

NO. 129C/M
COATING FAILURE
<7 HOURS

NO. 130
COATING FAILURE
<18 HOURS

Figure 1. Coating Failures under Conditions of 95-Percent Relative Humidity, 120° F
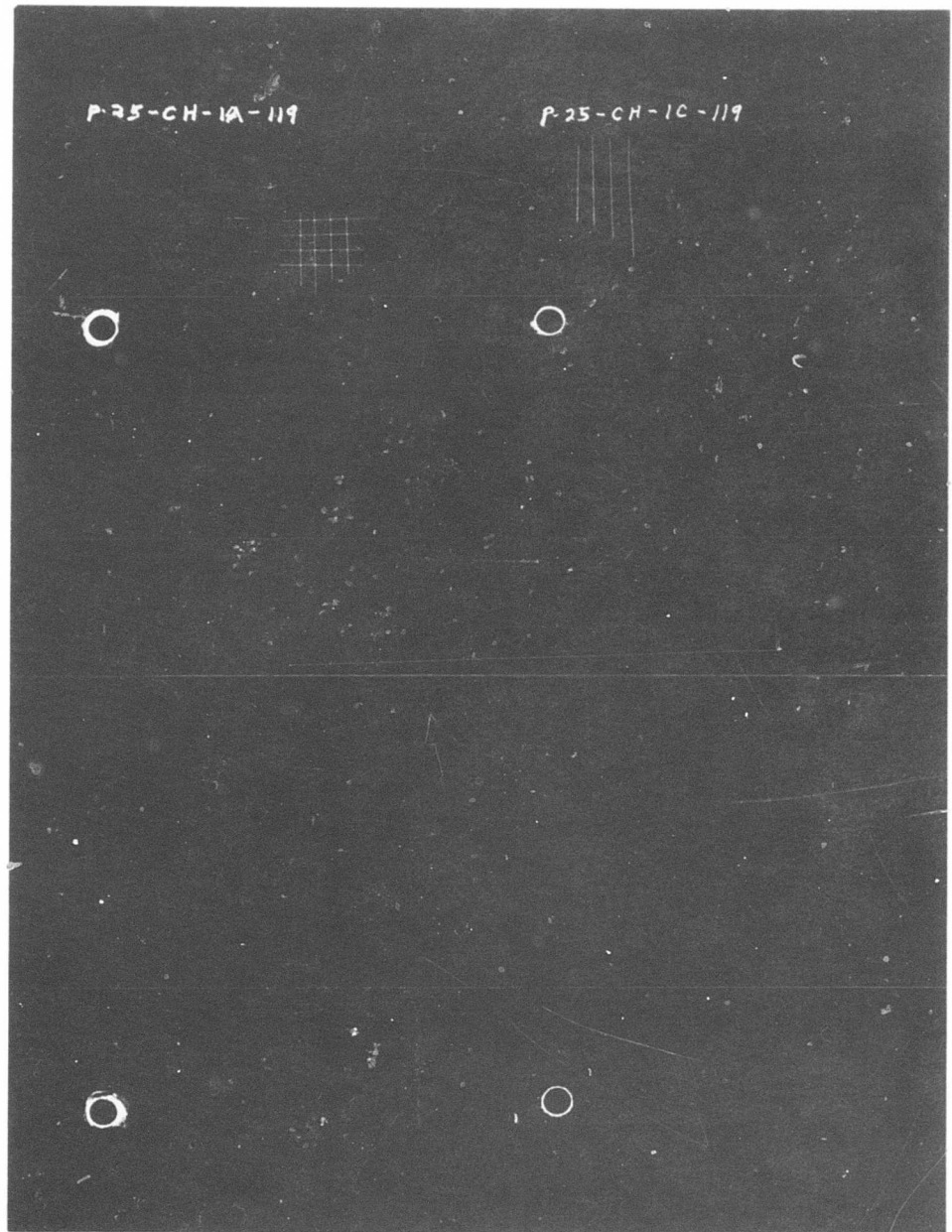
CONTROL (NO EXPOSURE)
SPECIMEN NO. 119 COATING

TESTED (EXPOSED 1344 HOURS)
SPECIMEN NO. 119 COATING

Figure 2.   No. 119 Coating Subjected to 120° F and 95-Percent Relative Humidity

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windshield was coated with the 119 material and cured. The coating had massive cracking which, in the sunlight, exhibited an unacceptable bright refraction capable of obstructing the pilot's view. A UH-1 panel coated with the 129C which was cured without cracking, but eventually crazed during outdoor weathering, is shown in Figure 3. The former had an Alon content and the latter had none.

f. Decision for a Change

Preliminary testing of Task II actually failed all of the four coatings developed by Marks for aircraft glazings although the hardness and abrasion-resistant properties remained unchanged. The requirements of Task II were changed in the contract to include Attagel-50 (TM) as a substitute filler for the Alon and develop a primer system for Plex II. (TM)

(TM) Attagel - trademark of Engelhard Minerals and Chemicals Corporation, Attapulgas, GA.

(TM) Plexiglas - trademark of Rohm and Haas, Philadelphia, PA.

Figure 3. UH-1 Panel Coated with 129C Crazed During Outdoor Weathering

SECTION V

MODIFICATION OF COATINGS

1. GENERAL

   a. Filler Substitution

   Task I concerned itself with Alon, an aluminum oxide filler, which was compatible with the Marks' coating systems. These systems were tested in Task II with the results tabulated in Appendix A, Table A-1. The crackings in coatings during cure were considered attributable to the Alon filler because the unfilled coatings did not exhibit the characteristic until they were environmentally tested.

   From the recommendations of A. Marks in report USAAMRDL-TR-75-22, the theory was expounded that coatings with needle-shaped crystals were superior to the approximate spherical-shaped particles (Alon), and that prolonged heating would not as likely result in cracking or crazing. A material trademarked Attagel-50 was cited as being a probable substitute for Alon. The Alon, incidentally, was no longer manufactured.

   b. Binder Substitution

   A fully hydrolyzed Elvanol® 71-30G polyvinyl alcohol had been used in all the coatings subjected to the environmental screening tests of Section III in this report. Although the 119 coating was initially microcracked, it did sustain the humidity test which destroyed the other coatings containing PVA. Various hydrolyzations and viscosities of PVA's were tested for crack resistance. The object was to find a PVA which wouldn't crack initially in a higher concentration (129C coating) and could be used in a lower concentration without cracking, and also pass the humidity test.

2. ATTAGEL COMPATIBILITY

   a. Solids Suspension Problem

   Obtaining a transparent gel from a water suspension of Attagel-50 through mechanical shearing, homogenization, and centrifuging was not successful.

® Elvanol – trademark of E. I. DuPont de Nemours Co., Wilmington, Del.

Pretreatment of the material with 0.04 percent by weight of tetrasodium pyrophosphate separated the material sufficiently to retain a suspension and obtain a clear gel. A secondary problem evolved in that the Attagel-50 and salt additive resulted in a pH of 9.5 to 10.00 (a strong electrolyte). The addition of the electrolyte to the PVA-silicic acid evidently reduced the pH to a point where the Attagel recoagulated. The consequence of the final mix was an unusable flocculation. The Alon mixes previously made had an advantage in that the gel was compatible with the remaining constituents and did not require chemical pretreatment to sustain a suspension.

b. Attempted Solutions

Several approaches were made toward solving the problem. Polar solvents, other than water, were used which possibly could retain the Attagel in suspension after the homogenization process without the use of a surfactant. Attempts were also made to reduce the pH of the highly alkaline Attagel-phosphate-water mixture with an acid treatment to have better compatibility with the silicic acid. A high order ionic salt with a lower pH (sodium citrate) was tried as a sequestering agent without success.

Both hydrocarbon and fluorocarbon surfactants were investigated and tested in recommended concentrations. In cases where the pH range wasn't great enough to encompass the pH of the phosphated Attagel, a one-half normal solution of ammonium citrate (previously found compatible with silicic acid in small amounts) was used as a buffer. The hydrocarbons and the more stable fluorocarbon surfactants failed in both the anionic and nonionic forms. Neither the use of wetting agents nor the reduction of pH value was successful in preventing refloculation of the Attagel.

A more universal surfactant, sodium carboxymethyl cellulose, had a compatibility pH range of 2 to 10 which was not expected to interfere with the phosphate or the silicic acid. One characteristic, however, was that a precipitate would occur in the presence of ethanol at a pH of 2.5. Because the silicic acid did have an ethanol component and did precipitate at a pH of 2.5, the silicic acid was diluted to a pH of 2.7 with the ethanol remaining in solution. Because the tetrasodium pyrophosphate had a pH very close to 10, a lower pH defloculant, sodium hexametaphosphate, was employed. The predicted compatibility chart of all proposed coating components is shown in Figure 4. The system did not prevent refloculation of the Attagel solids.
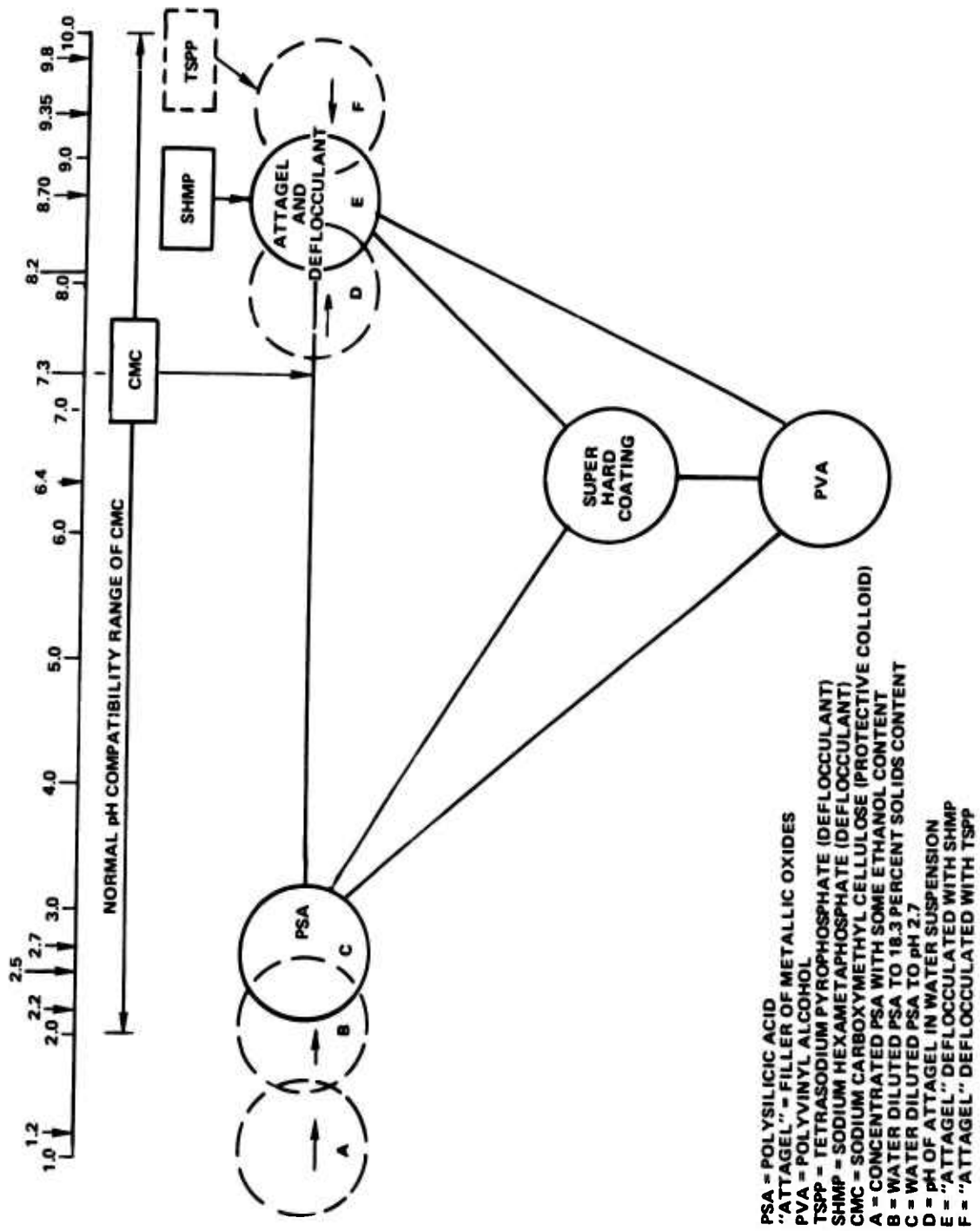
Figure 4. Predicted Compatibility Chart for an Attagel-Filled Superhard Coating

PSA = POLYSILICIC ACID
"ATTAGEL" = FILLER OF METALLIC OXIDES
PVA = POLYVINYL ALCOHOL
TSPP = TETRASODIUM PYROPHOSPHATE (DEFLOCCULANT)
SHMP = SODIUM HEXAMETAPHOSPHATE (DEFLOCCULANT)
CMC = SODIUM CARBOXYMETHYL CELLULOSE (PROTECTIVE COLLOID)
A = CONCENTRATED PSA WITH SOME ETHANOL CONTENT
B = WATER DILUTED PSA TO 18.3 PERCENT SOLIDS CONTENT
C = WATER DILUTED PSA TO pH 2.7
D = pH OF ATTAGEL IN WATER SUSPENSION
E = "ATTAGEL" DEFLOCCULATED WITH SHMP
F = "ATTAGEL" DEFLOCCULATED WITH TSPP

NORMAL pH COMPATIBILITY RANGE OF CMC

Two other forms of Attagel were examined. One was a coarser grade which had been refined in a different manner and the other, a commercially prepared liquid suspension of Attagel which had a phosphate content. It was hoped that the difference in refinement of the former could yield a small fraction of suspension without chemical treatment. No suspension remained after an initial centrifuging. The liquid form offered some processing improvement in that the material could be centrifuged directly without homogenization, although several centrifugings were necessary and the yield appeared smaller.

3. POLYVINYL ALCOHOL SUBSTITUTION

Polyvinyl alcohols were available in various viscosities and hydrolyzations. The Elvanol 71-30 was a medium viscosity fully hydrolyzed PVA. Theoretically, a partially hydrolyzed material could offer more flexibility and retain sufficient cross-linking to give water resistance. Other viscosities would affect flow and therefore coating thickness variations which could affect the cracking phenomenon during cure.

As a comparative test, the PVA's of Table 7 were all formulated in a code 129C coating (did not contain a filler) and cured at 180 deg F for 19 hours on an FA5 primed stretched Plex 55 substrate. All cracked to some degree except the Vinol V-523.®

TABLE 7.   CRACK RESISTANCE RANKING OF POLYVINYL ALCOHOLS CURED IN 129C COATING FOR 19 HOURS AT +180 DEG F

Product	Description	Rank [*]
Vinol V-523	Partially hydrolyzed, medium viscosity	1
Vinol V-205	Partially hydrolyzed, low viscosity	2
Gelvatol 1-30 ®	Fully hydrolyzed, medium viscosity	2
Elvanol 71-30	Fully hydrolyzed, medium viscosity	3
Vinol 107	Fully hydrolyzed, medium viscosity	4
Vinol 350	Fully hydrolyzed, high viscosity	5
Vinol 325	Fully hydrolyzed, medium viscosity	6

*Rank 1 = best crack resistance; rank 6 = poorest crack resistance.

® Vinol – trademark of Air Products and Chemicals, Inc., Piscataway, N. J.
® Gelvatol – trademark of Monsanto Polymers and Petrochemicals, St. Louis, MO.

The Vinol V-523 was formulated into a test batch of a modified 119 coating which contained silicon dioxide as a filler. Elvanol 71-30G was formulated into a control batch in place of the Vinol product. Both were cured 17 hours at +180° F on FA5 primed stretched Plex 55 panels. Both microcracked during cure.

The 119 coating had an advantage in being able to pass the humidity test by virtue of its not having a high percentage of PVA in the coating, although the coating did exhibit premature cracking during cure using the Elvanol 71-30.

Table 8 lists component proportions used for finding a threshold of PVA content between 5 and 15 percent solids which would pass the humidity test in the 129C coating. These percentages were based on the 119 and 130 coatings sustaining themselves in the high-humidity environment for an extended period of time.

Calculating for the modification of the 129C coating by removing some of the PVA content, batches were prepared as shown in Table 8.

Panels were poured on FA5 primed stretched Plex 55 and cured at +190 deg F for 19 hours. All coatings were initially cracked. Specimens from them were subjected to the 95-percent relative humidity at +120° F. The 11 and 13 percent of PVA solids showed evidence of the typical blistering within 24 hours. The 5, 7, and 9 percent specimens remained in the environment 25 days without blistering. Ten percent solids of PVA would seem to be a maximum coating content without accruing humidity failures.

TABLE 8. MODIFIED 129C FORMULATIONS

Percent PVA solids	5	7	9	11	13	Unmodified 129C formulation 30
Parts by weight in grams						
15 percent PVA/ H_2O Sol	7.30	10.26	13.19	16.10	19.00	40.00
Polysilicic acid	56.00	56.00	56.00	56.00	56.00	56.00
H_2O	36.70	33.74	31.00	27.90	25.00	-0-
Total	100	100	100	100	100	100

SECTION VI

PRIMERS

1. GENERAL

All comparative testing of coatings was performed on stretched Plex 55 which had been primed with the FA5 primer. Because the FA5 and FA6 primers previously recommended for stretched Plex 55, as-cast Plex 55, Plex II, and polycarbonate contained between 98 and 99 percent glacial acetic acid, two problems presented themselves. First, the material was difficult to handle in open pours on a large scale. Secondly, the acid crazed the Plex II and decreased the impact resistance of polycarbonate. A tertiary problem was posed in finding a substitute for the acetic acid because the Formvar 7/95E Ⓜ component had a limited number of solvents in which it could be dissolved, and most, if not all, attacked these substrates in a range from slight to complete degradation.

2. SUBSTITUTION OF ALCOHOL BLEND FOR ACETIC ACID

One material which had been compounded as a direct substitution was methyl butynol. Preliminary tests showed the concentrated material to be compatible with the substrates and coatings, with the exception of Plex II. The material had a very low degree of toxicity and a flash point slightly higher than isopropyl alcohol.

To obtain compatibility with Plex II substrates, blends of ethanol and methyl butynol were made with a Formvar 7/95E additive. Dilution of the methyl butynol was a maximum of 40 percent ethanol and 60 percent methyl butynol before the Formvar came out of solution. These blends clouded the Plex II. A pour of methyl butynol alone on Plex II in a low relative humidity had caused some rule-line attack at the edges where the methyl butynol had not flashed off as rapidly; otherwise, no clouding occurred. By pouring in a controlled humidity of 35 percent, the methyl butynol/ethnol/Formvar 7/95E was applied without cracking.

One panel each of polycarbonate, stretched Plex 55, and Plex II had been cleaned and primed. The primer was methyl butynol/ethanol 60-40 with Formvar 7/95E. The primer was cured 1/2 hour at room temperature and 2 hours at +180 deg F.

Ⓜ Formvar - trademark of Monsanto Polymers and Petrochemicals Co., St. Louis, Mo.

A modified 119 coating was prepared:

$$PSA = 80.9 \text{ grams}$$

$$\text{Vinol 523 PVA} = 9.8 \text{ grams}$$

$$\text{Nalcoag}^{®} \text{ 1034A } SiO_2 = 10.9 \text{ grams}$$

$$H_2O = 97.0 \text{ grams}$$

The coating was poured on all three substrates and air cured 1/2 hour and 20 hours between +180 and 190° F. The results are shown in Table 9.

The three panels were cut and specimens placed in 120° F, 95 percent relative humidity for 4 days. The results appear in Table 10.

TABLE 9. CONTROL TESTS ON MODIFIED 119 COATING

Panel no.	Substrate	Appearance	Adhesion	Hardness
75	S/55	Massive fine cracking	Good	Good
76	Plex II	Flaking of coating	Unacceptable	Unacceptable
77	Polycarbonate	No cracking, but cloudy	Marginal	Acceptable

TABLE 10. HUMIDITY TESTS ON MODIFIED 119 COATING

Panel no.	Substrate	Appearance	Adhesion	Hardness
75	S/55	Developed irridescence	Acceptable	Acceptable
76	Plex II	Developed irridescence	-	-
77	Polycarbonate	Developed light cracking	40 percent	Acceptable

®Nalcoag – trademark of Nalco Chemical Co., Chicago, Ill.

Figure 5 is a microphotograph of the fine cracking.

Figure 6 is a microphotograph of the flaking on Plex II showing the radical displacement of the coating with respect to the primer.

Further microscopic examination revealed that:

1. Foreign particles or bubbles tend to propagate a crack (see Figure 7).

2. The primer apparently did not flake (see Figure 8).

3. The gap between flakes being larger than a crack indicates contraction of the coating (see Figure 8).

4. The primer covers and fills much of the substrate surface abnormalities (see Figure 9).

5. Rule lines (Figure 10) are theorized as being caused by vortex currents through the cross-sectional thickness of the film during the evaporation of the solvents.

Figure 5. Microcracking of Panel No. 75 Modified 119 Coating with SiO_2 and Partially Hydrolyzed PVA on Stretched Plex 55 with Methyl Butynol/Ethanol/Polyvinyl Formal

MARK-OFF TRANSFERRED
TO COATING

SCRATCHES
ON PRIMER
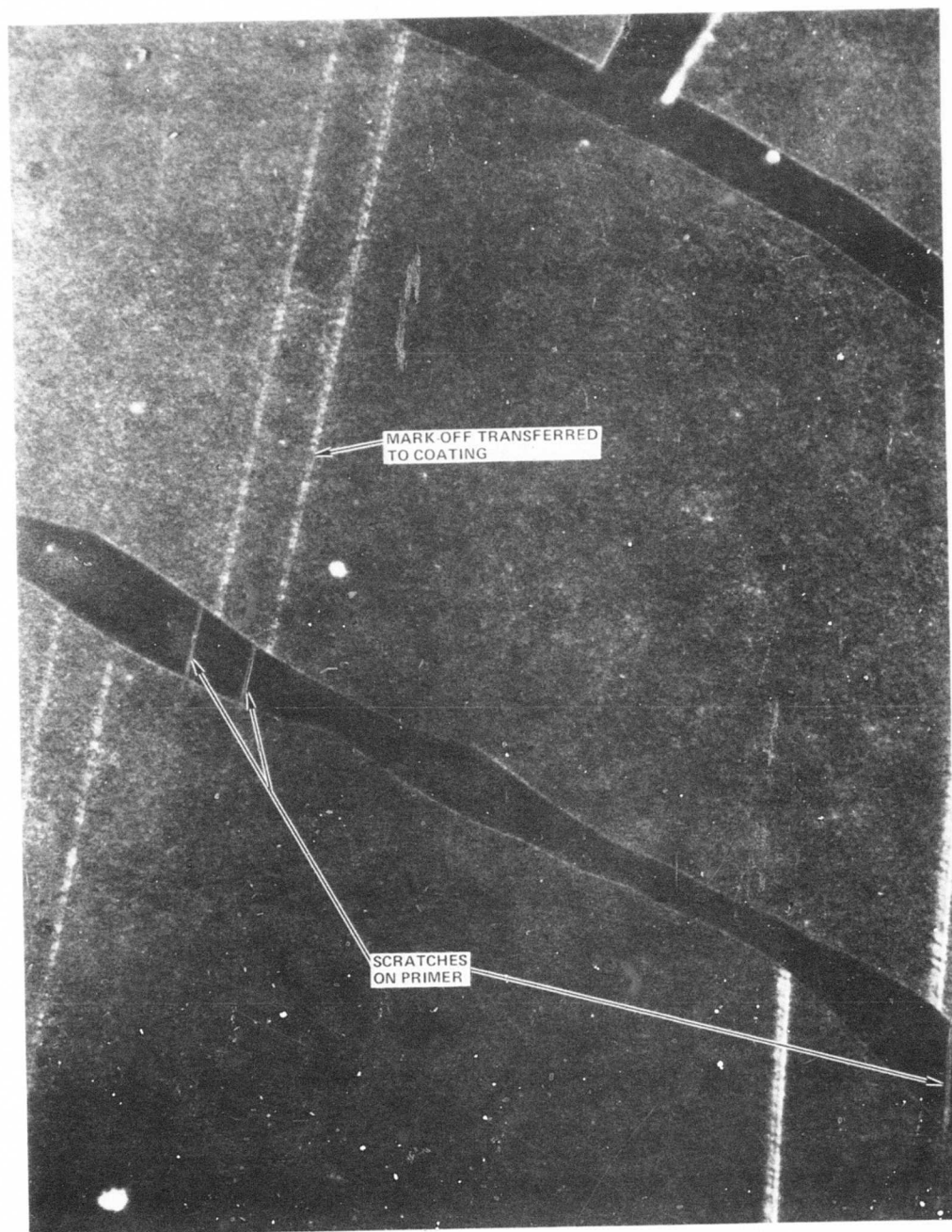
Figure 6. Flaking of Panel No. 76 Modified 119 Coating with SiO_2 and
Partially Hydrolyzed PVA on Plex II Substrate and Methyl
Butynol/Ethanol/Polyvinyl Formal

39
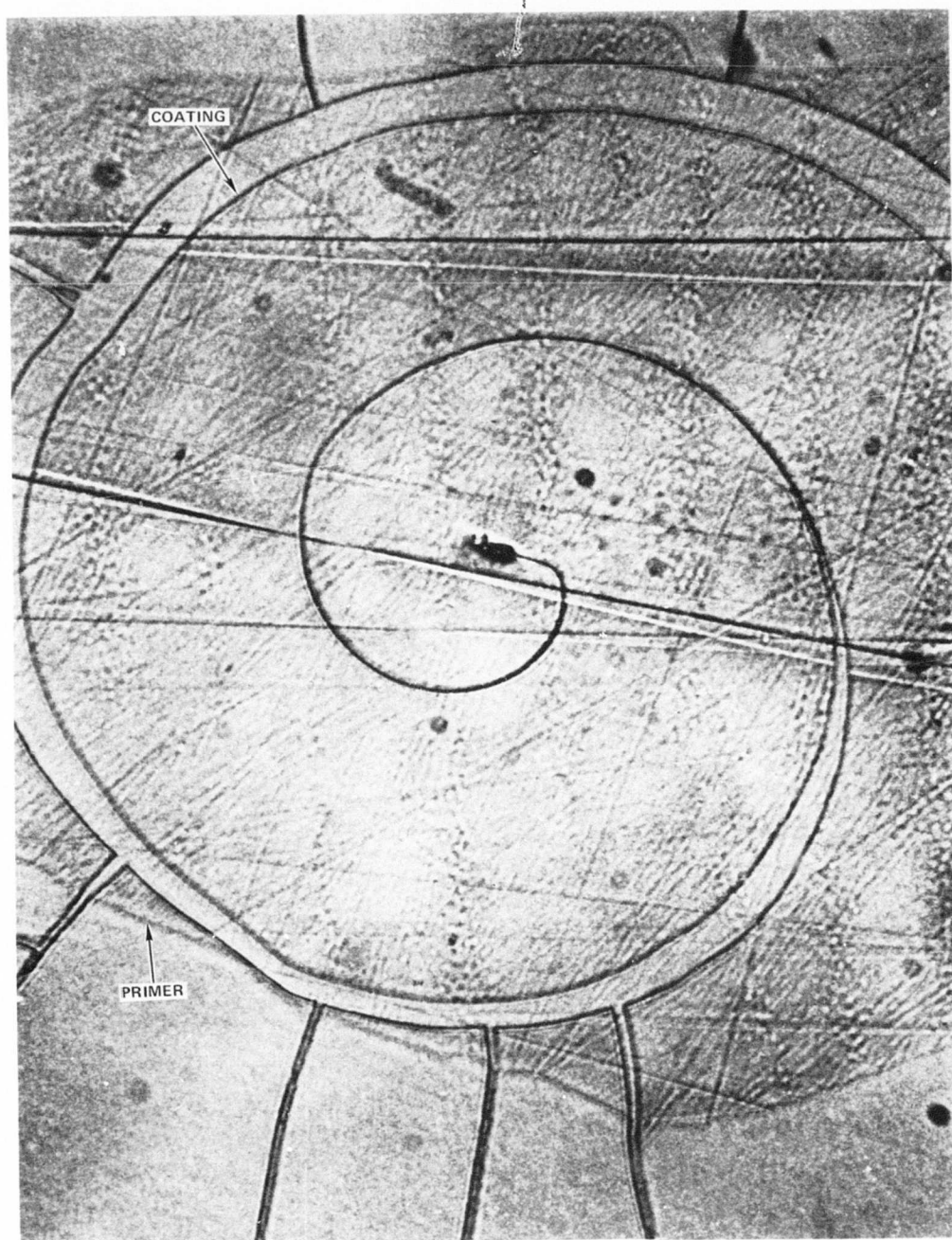
Figure 7.   Propagation of Crack from Locus of Bubble or Foreign Particle
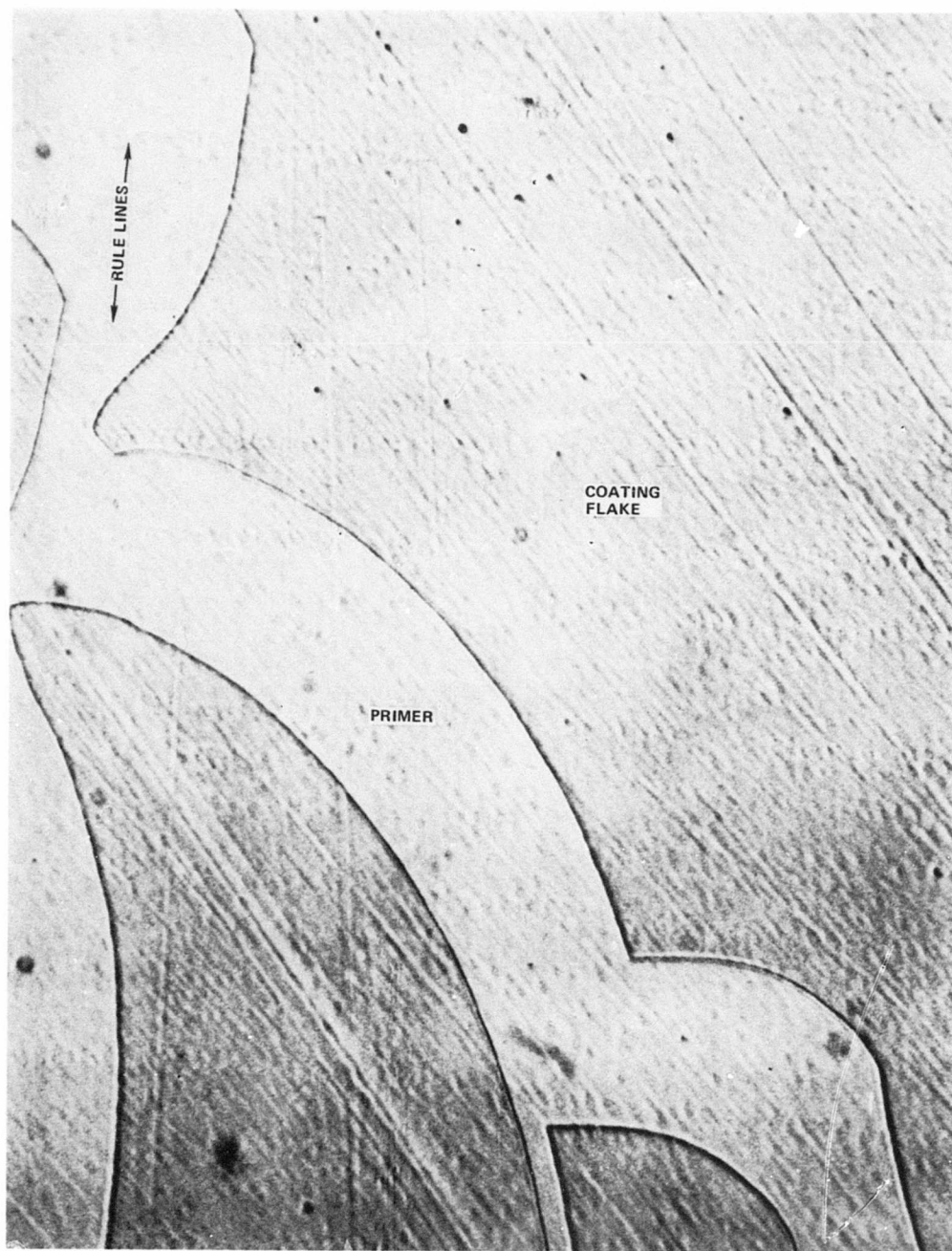
Figure 8. Microphotograph of General Flaking Showing the Primer Intact

41
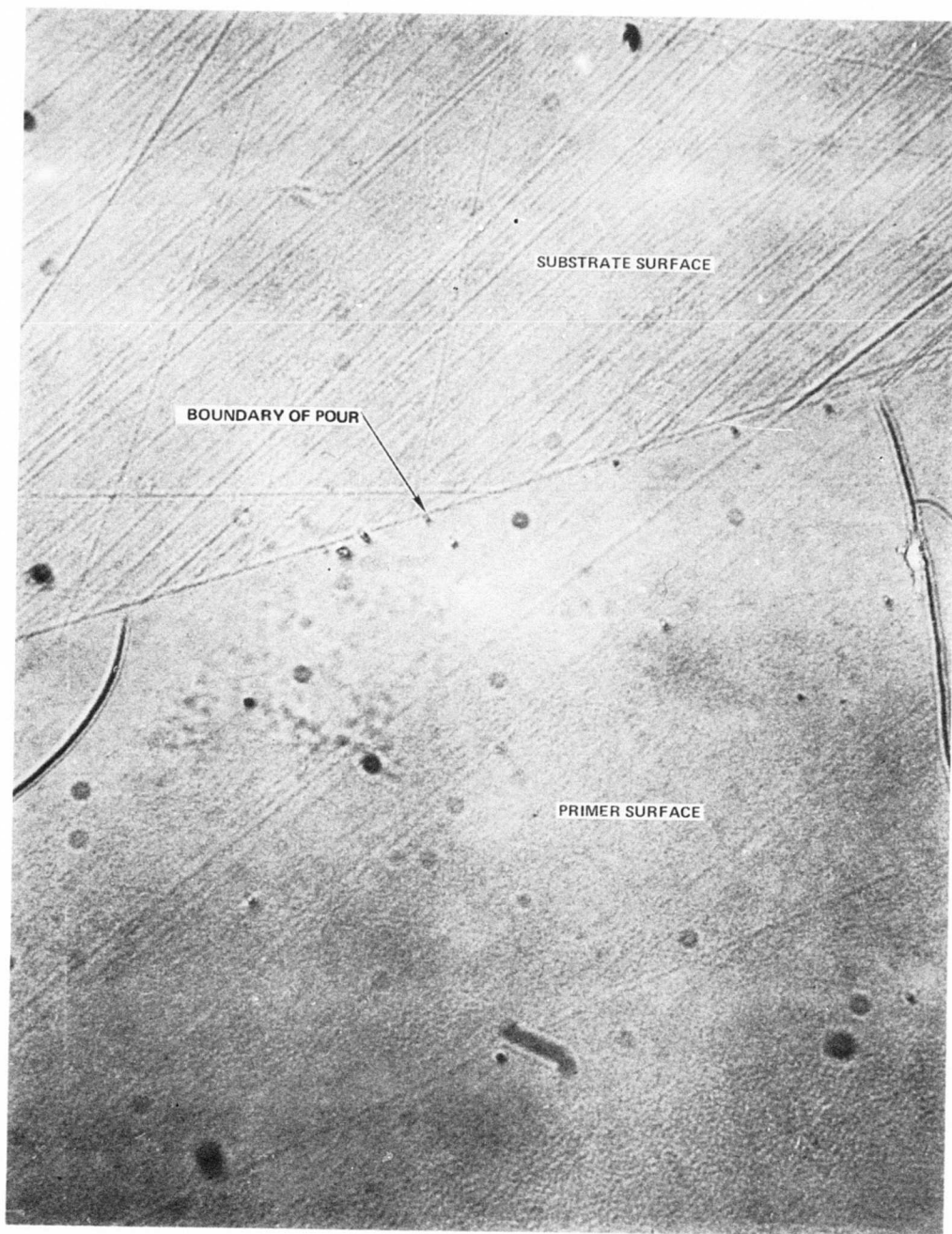
Figure 9.   Microphotograph of Substrate and Primer Surfaces

42
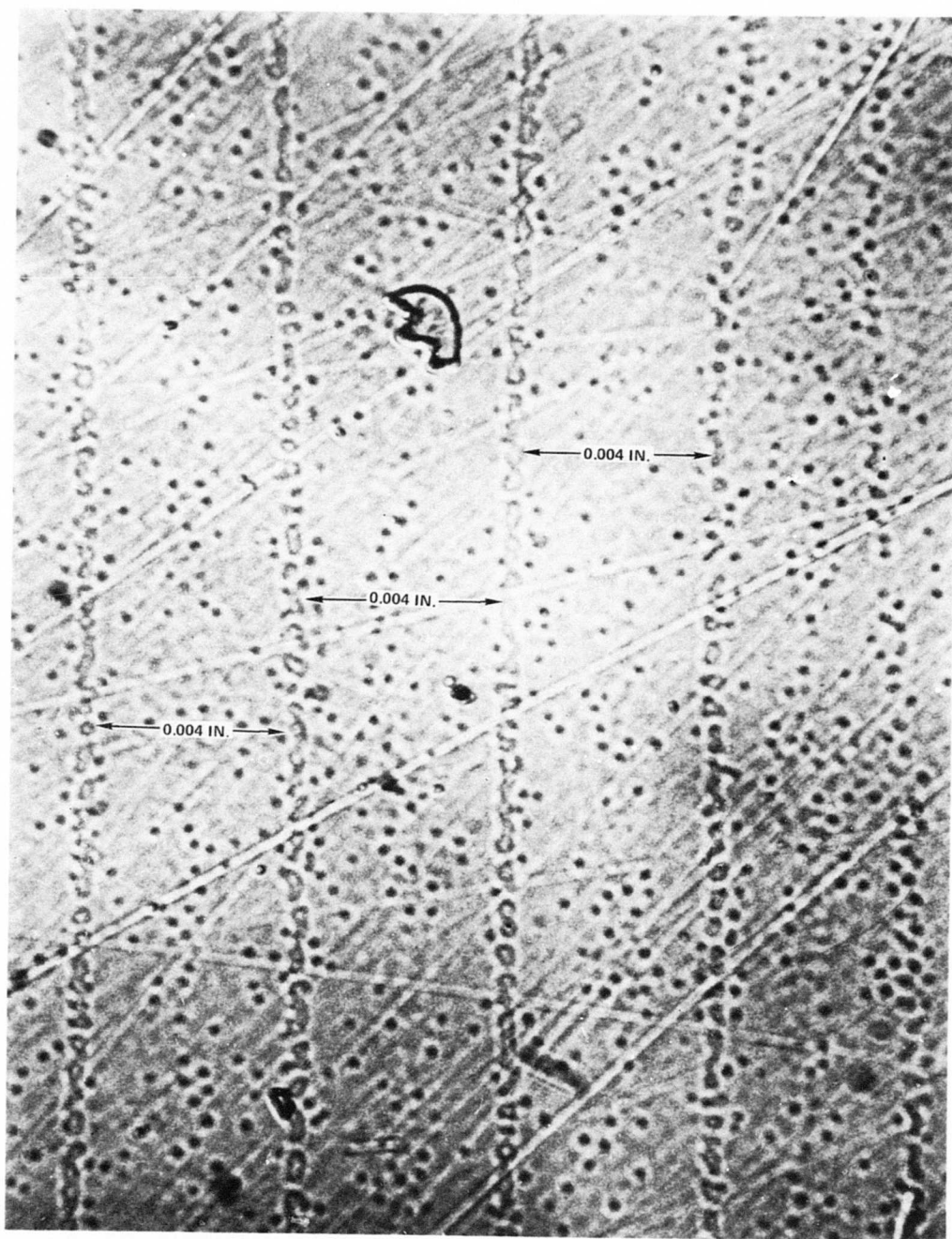
Figure 10. Rule Lines in Primer

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SECTION VII

DECISION TO TERMINATE TASK II

Task II was revised to include material substitutions for both the primer and the coating systems. Success did not appear imminent because of failures after a short-term exposure to a hot, humid environment. The alcohol-based primer adhered marginally to polycarbonate and well to stretched Plex 55 and Plex II. In the case of Plex II, the coating did not adhere to the primer during cure. The Attagel was found to be incompatible with the Marks system. The silica substitution for the no longer available Alon alumina appeared to be compatible.

Task II was terminated in favor of Task III which was redirected toward the development of a new coating based on polysilicic acid chemistry. All other materials would be subject to change.

SECTION VIII

COATING SYSTEM CHANGE

1. GENERAL

   a. Purpose

   The purpose of this change was to ultimately formulate a flightworthy coating system which would be a best effort toward solving the deficiencies of the current superhard coatings systems.

   b. Approach

   The approach was to retain a polysilicic acid system and choose other film forming materials which would be theoretically compatible with the system.

2. CHEMISTRY OF ALKYL SILICATES

   The explanation of the forming of SiO_2 crystallites from tetraethyl orthosilicate in Section II, paragraph 2.c. is a basic concept, but the process of hydrolysis is more complex.[a] Crystalline silica in the form of SiO_2 is never really produced. Many intermediate species of polysilicates are formed during hydrolysis. As the reaction proceeds, the polysilicates grow in molecular weight and chain length, until most or all of the ethyl groups are driven off and a nonlinear network of -Si-O-Si- remains.

   This chemical process of hydrolysis is the basis for application of ethyl silicate products as binders. By partially hydrolyzing tetraethyl orthosilicate under carefully controlled conditions, a stable mixture of polysilicate "pre-polymers" can be made. These materials can be stored for a limited period of time and when ready for use as binders, can be hydrolyzed to completion by adding the proper amount of water and changing the pH to an unstable range by using a gel agent. Most of the water for 100 percent hydrolysis is present in these binders; a change in pH will push the reaction to completion.

   ---

   [a] Discussion of chemical process of hydrolysis adapted from technical literature of Stauffer Chemical Co., New York, N.Y.

The stoichiometric equation for partial hydrolysis is as follows:

$$Si(OR)_4 + 2xH_2O \xrightarrow{H^+ \text{ or } OH^-} \left[Si(OR)_{4(1-x)} (O)_{2x} \right] + 4x\ ROH$$

<div align="right">polymer</div>
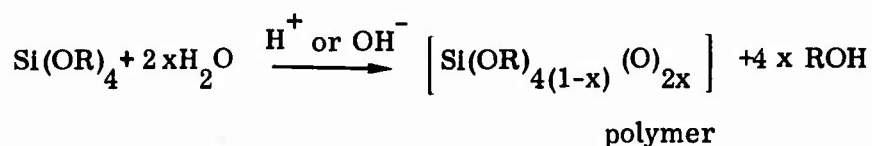
where

$$x = \frac{\text{Degree (percent) of hydrolysis}}{100}$$

$R = C_2H_5$ (ethyl group) for ethyl silicate.

It is imperative that a small amount of acid or base be added to catalyze the hydrolysis.

The mechanism of hydrolysis of ethyl (or other alkyl = R) silicate is as follows:

Acid hydrolysis:

$$-\overset{\textstyle |}{\underset{\textstyle |}{Si}}-OR + H_2O \xrightarrow{H^+} -\overset{\textstyle |}{\underset{\textstyle |}{Si}}-OH + ROH$$

Mechanism:

$$-\overset{\textstyle |}{\underset{\textstyle |}{Si}}-\overset{H^+}{OR} \rightarrow -\overset{\textstyle |}{\underset{\textstyle |}{Si}} - \overset{H}{\underset{\overset{+}{O}}{O}} - R \rightarrow -\overset{\textstyle |}{\underset{\textstyle |}{Si}} + HOR\uparrow \rightarrow -\overset{\textstyle |}{\underset{\textstyle |}{Si}} - OH + H^+$$
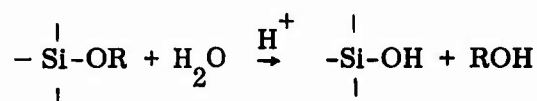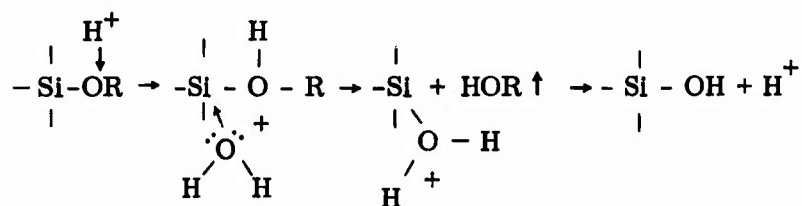
In this reaction, a silicic acid ester is generated, along with an alcohol, which leaves the reaction. A hydrogen (or Lewis acid) ion (H$^+$) is consumed and regenerated with no net loss or gain, thus perpetuating the reaction.

This same reaction takes place with a base:

Base hydrolysis:

$$-\underset{|}{\overset{|}{Si}} - OR + H_2O \quad \overset{OH^-}{\longrightarrow} \quad -\underset{|}{\overset{|}{Si}} - OH + ROH$$

Mechanism:

$$-\underset{\overset{\nwarrow}{OH^-}}{\overset{|}{Si}} - OR \rightarrow -\underset{\overset{\searrow}{OH}}{\overset{|}{Si}} \bar{-} OR \rightarrow -\underset{|}{\overset{|}{Si}} - OH + \bar{O}R \quad \underset{H_2O}{\boxed{}} \quad ROH + \bar{O}H \uparrow$$
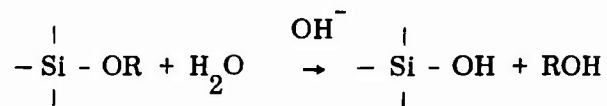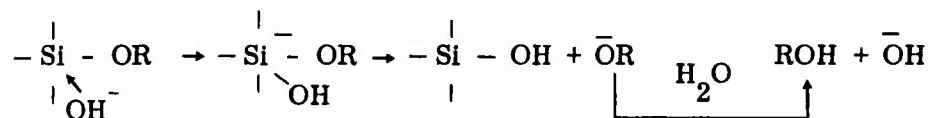
For alkyl silicate polymers to form, the following condensation reactions must occur:

Acid condensation:

$$-\underset{|}{\overset{|}{Si}} - OH + -\underset{|}{\overset{|}{Si}} - OH \quad \overset{H^+}{\longrightarrow} \quad -\underset{|}{\overset{|}{Si}} - O - \underset{|}{\overset{|}{Si}} - + H_2O$$

Mechanism:

$$-\underset{\underset{H^+}{\overset{\nearrow}{}}}{\overset{|}{S}} - OH \rightarrow -\underset{\underset{-Si-OH}{\overset{|}{}}}{\overset{|}{Si}} - OH_2 \overset{+}{} \rightarrow \underset{-Si-}{\overset{-Si-}{\underset{|}{\overset{|}{O}} - H}} \overset{+}{} + H_2O \quad -\underset{|}{\overset{|}{Si}} - O - \underset{|}{\overset{|}{Si}} - + H^+$$
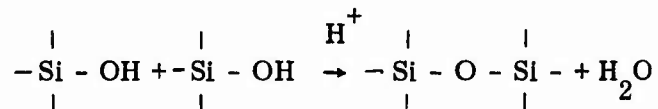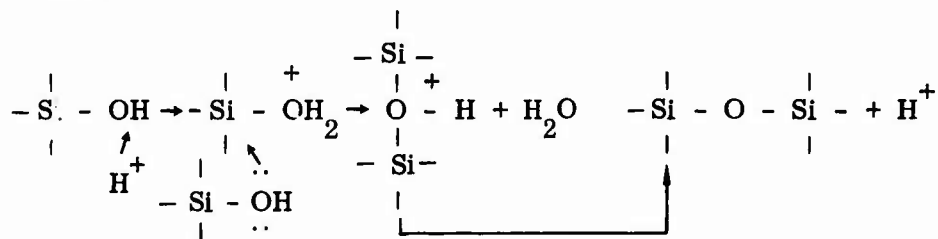
In this reaction, two silicic acid esters react to form a dimer (or higher polymer), generating H_2O, which continues the hydrolysis reaction. Again there is no net loss or gain of the H^+ ion.

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Similarly:

Base condensation:

$$-\overset{|}{\underset{|}{Si}} - OH \ + -\overset{|}{\underset{|}{Si}} - OH \quad \overset{OH^-}{\longrightarrow} \quad -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - \ + H_2O$$

Mechanism:

$$-\overset{|}{\underset{|}{Si}} - OH \overset{}{\underset{OH^-}{\longrightarrow}} -\overset{|}{\underset{|}{Si}} - O^- + H_2O \qquad -\overset{|}{\underset{|}{Si}} - OH \rightarrow -\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - \ + OH^-$$

$$\longrightarrow -\overset{|}{\underset{}{Si}} - O^-$$
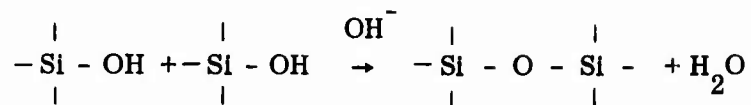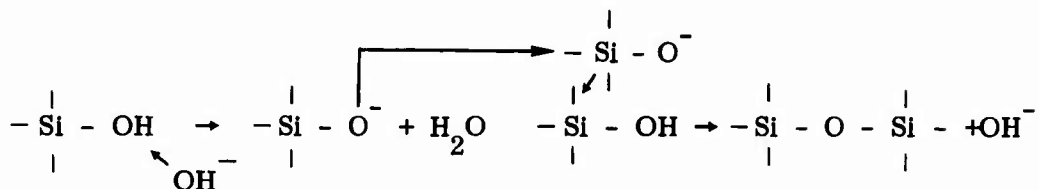
3. COATING DEVELOPMENT PLAN

The plan used to develop the final coating is shown in Figure 11.
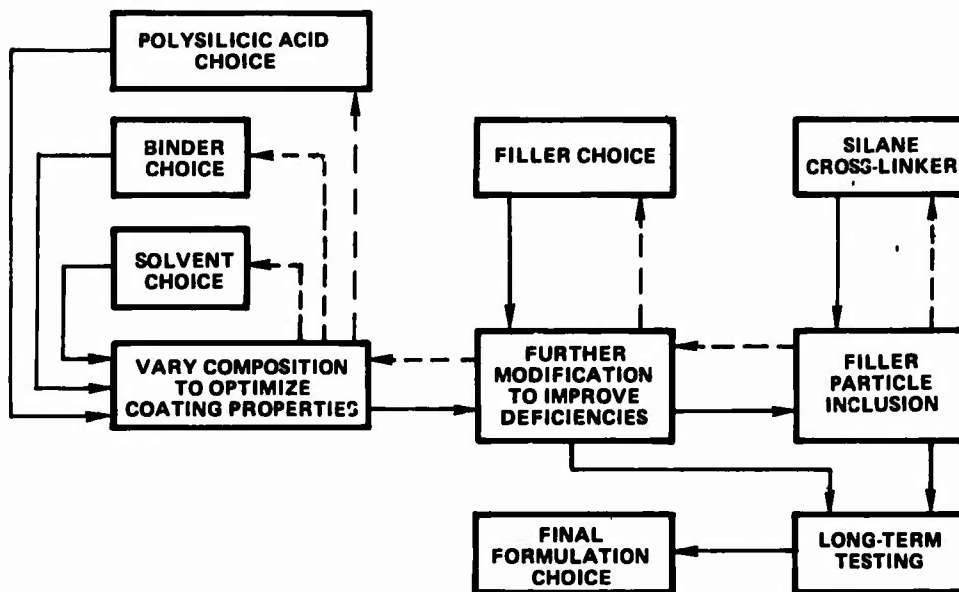
Figure 11. Coating Development Plan

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4. POLYSILICIC ACID

Various sources of polysilicic acid were considered as shown in Table 11. All would have to be reacted with water and a Lewis acid or base. Previous work has been done, primarily with tetraethyl orthosilicate, which forms a brittle, hard film. A commercially developed coating utilizing this type system had the disadvantage of a reduction in hardness after being subjected to humidity. Formulations without surfactants resulted in a better resistance to humidity, but cracked upon cure.

In an attempt to provide more flexibility, the remaining materials in Table 11 were tried. The H-4, H-6, and TNPS materials contained other proprietary materials which affected their direct substitution for the silicic acid derived from the tetraethyl orthosilicate. The silicic acids derived from the quaternary aluminum silicates were unsatisfactory because of the residual aluminum hydroxide gels which would tend to form.

The final choice of polysilicic acid sources was a blend of the Silbond® (99-percent pure TEOS) and the Silbond H-4.

5. BINDER CHOICE

None of the coatings which utilized PVA survived the humidity test adequately. Another binder was sought which would, in theory, be more hydrolytically stable. A literature search produced the choice of a water soluble amine terminated acrylic polymer with properties of:

Viscosity	4000-7000 cps
Color	5 max (Gardner Scale)
pH	5-5.6

Because XD-7080,® co-cured with a bisphenol-A base resin, was reported to react in coatings which exhibited good ultraviolet and chemical resistance, could be reduced in water, had a long work life, and was known to have good adhesion to a wide range of substrates, it was chosen as a substitute for PVA. Because the material is obtained in the form of a hydrochloric acid salt of the amine terminated polymer, its pH would be expected to be compatible with the polysilicic acid solutions of low pH.

®Silbond – trademark of Stauffer Chemical Co., New York, N.Y.

®XD-7080 – trademark of Dow Chemical Co., Midland, Mich.

TABLE 11. POSSIBLE SOURCES OF SILICIC ACID

Supplier	Commercial name	Chemical composition	Density (lb/gal)	Silica [weight percent silicic acid (SiO$_2$)]	pH (at 25 deg C)
Philadelphia Quartz Co.	Quram 3365 ™	Quaternary ammonium silicate	9.8	20.0	11.3
Philadelphia Quartz Co.	Quram 220 ™	Quaternary ammonium silicate	11.6	44.0	11.1
Stauffer Chemical Co.	Silbond TNPS (90 percent)	Tetra N-propyl silicate	7.6	22.8	0.05*
Stauffer Chemical Co.	Silbond pure (99 percent)	Tetraethyl orthosilicate	7.8	28.5	0.001*
Stauffer Chemical Co.	Silbond H-4	Prehydrolyzed ethyl polysilicate	7.6	18.0	0.015*
Stauffer Chemical Co.	Silbond H-6	Prehydrolyzed ethyl polysilicate	8.3	18.3	0.055*

™ - trademark of Philadelphia Quartz Co., Philadelphia, Pa.

*Weight percent HCl maximum.

An acrylic binder, Polytex 910(TM) with Polylink 980,(TM) was tried with the PSA, but it coagulated with the PSA and was abandoned.

6. SOLVENT CHOICE

Solvent evaporation controls the setting time of most coatings. The solvent must remain in the coating long enough to allow flow sufficient to produce adequate adhesion, gloss, and leveling. It must evaporate fast enough to prevent sagging and inadequate film thickness.

The relationship between evaporation rate and solvency is always critical with blends of different solvent types. Such is the case for superhard coating formulations. Besides the organic solvents present in the composition, there are also water and acetic acid, which should be taken into consideration. Solvents rarely evaporate at the same rate; therefore, the composition and resulting solvency change as the blend evaporates. Film properties can vary widely because of this phenomenon. Retained solvent can affect coating properties such as clarity, gloss, adhesion, water resistance, and hardness.

Solvent evaporation rates were obtained in accordance with the Test Method in Appendix C.

Because different solvents are contained in the coating raw materials list, the evaporation rates realistically concern mixtures rather than separate acids, alcohols and water. Table 12 concerns volatile losses of three different polysilicic acid compositions alone with the XD-7080/DER-332(TM) binder. The associated graph of Figure 12 plots these figures along with some of the earlier unfilled coatings using these constituents and comparing them to Abcite.(TM)

By blending coating constituents in various ratios which will tend toward a constant slow evaporation rate, coating stresses (which cause cracking) can be reduced.

Essentially, the choices of solvents are predetermined, to a great extent, by those contained in the proprietary constituents. Dilutions with water, alcohols, or other compatible solvents can adjust the curve within limits and improve flow and cure characteristics.

(TM)Polytex 910 and Polylink 980 - trademarks of Celanese Coatings Co., Louisville, Ky.

(TM)XD-7080/DER-332 - trademark of Dow Chemical Co., Midland, Mich.

(TM)Abcite - trademark of E. I. DuPont De Nemours, Co., Inc., Wilmington, Del.

TABLE 12. VOLATILE LOSS OF POLYSILICIC ACIDS AND XD-7080/DER-332 BINDER

		Volatile content (percent)	Volatile components lost in:		
			30 min (percent)	60 min (percent)	90 min (percent)
Raw material	Epoxy binder	36.4	37.1	39.8	41.2
	Polysilicic acid - A	71.5	57.3	71.3	76.9
	Polysilicic acid - B	81.8	72.2	88.1	89.3
	Polysilicic acid - C	82.4	77.7	87.4	88.8
Superhard coating	Formulation no. 129	88.5	33.9	55.3	74.6
	Formulation no. 130	88.5	33.9	55.4	72.3
	Formulation no. 136	88.7	32.7	54.3	72.0
	Formulation no. 147	92.4	47.1	71.4	88.2
	Abcite (Code-705)	90.3	39.9	66.0	86.4

7. FILLERS

Two fillers survived the screening of the many materials listed in Appendix B. Those in the listing were checked for compatibility with acidic neutral and basic environments as well as their ability to form a clear gel during centrifuging. The most probable were the Cab-O-Sil (TM) EH-5 and the Aluminum Oxid "C".(TM) Both were obtained in their submicron form through a "fuming" process. The latter is claimed to be very similar to the Alon which is no longer manufactured. The Cab-O-Sil M-5 (TM) of a slightly larger granule was also used to obtain curves which would provide the percentage of retained filler versus average particle size for various centrifuge speeds. The filler properties eliciting the most interest are shown in Table 13.

Reproducibility of filler concentrations was obtained by standardizing the shearing speed (Waring blender), time, and percentage of solids added to water by

(TM)Cab-O-Sil EH-5 - trademark of Cabot Corp., Boston, Mass.

(TM)Aluminum Oxid "C" - trademark of Degussa Inc., Teterboro, N. J.

(TM)Cab-O-Sil M-5 - trademark of Cabot Corp., Boston, Mass.
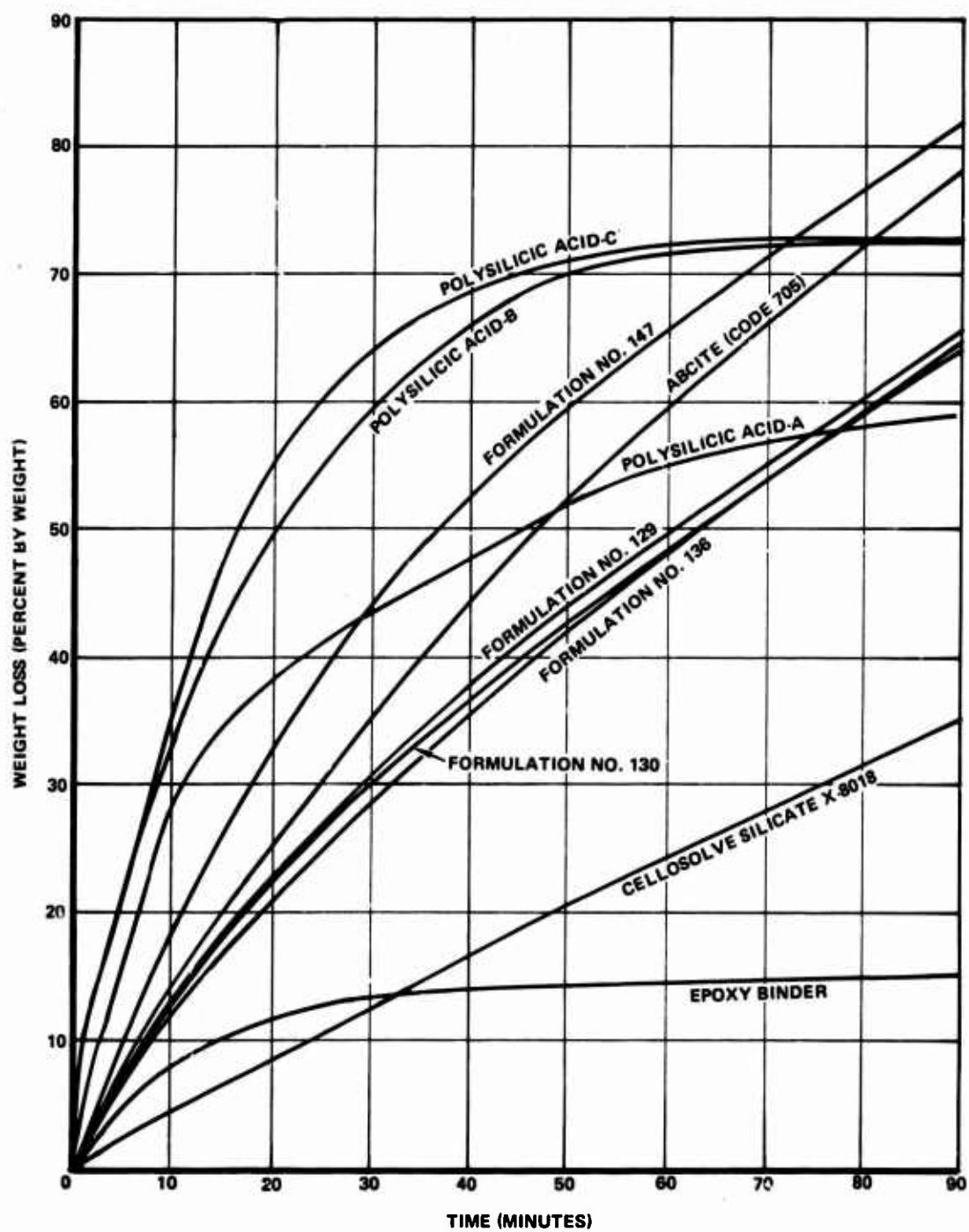
Figure 12. Evaporation Rate Analysis

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TABLE 13.   PROPERTIES OF VARIOUS FILLERS

	Aluminum Oxid "C"	Alon	Fumed silica M-5	Fumed silica EH-5
BET surface area (m^2/gm)	100 ±15	100	200 ±15	390 ±40
pH (4 percent aqueous suspension)	4.0-5.0	4.1-4.6	3.5-4.2	3.5-4.2
Nominal particle size (microns)	0.020	0.030	0.014	0.007
X-ray structure	Primarily gamma	90 percent gamma	Amorphous	Amorphous
Surface charge	+	+	-	-

weight.   The percentage of solids used for this determination was 4 percent.
Curves for centrifuge speeds of 4500 and 9000 rpm were established by running
filler suspensions of different particle sizes for various time spans at these
velocities and weighing the solids content of the remaining suspension.   The
latter was accomplished by weighing a small portion of the suspension, evaporating
all the water, and weighing the residue.   Figures 13 and 14 show the results
of these determinations.

Considering the nominal particle sizes from Table 13, the curves of Figures 13
and 14, and a centrifuge time of 15 minutes, the plot of percentage of retained
filler versus nominal particle size resulted in a straight line, independent of
other variables for a given centrifuge speed as shown in Figure 15.   By extend-
ing the same slope for the one point of Aluminum Oxid "C" at 4500 rpm, parallel
slopes for intermediate centrifuge speeds can be estimated.

Using the standard equation for a straight line, $Y = mx + b$, the Y intercept of
the 9000 rpm/15 min curve is 132 percent and is equal to b.   The slope was
calculated to be -6500; therefore, the equation becomes $Y = -6500x + 132$ for a
centrifuge speed of 9000 rpm.   The "Y" intercept, however, will vary with speed.
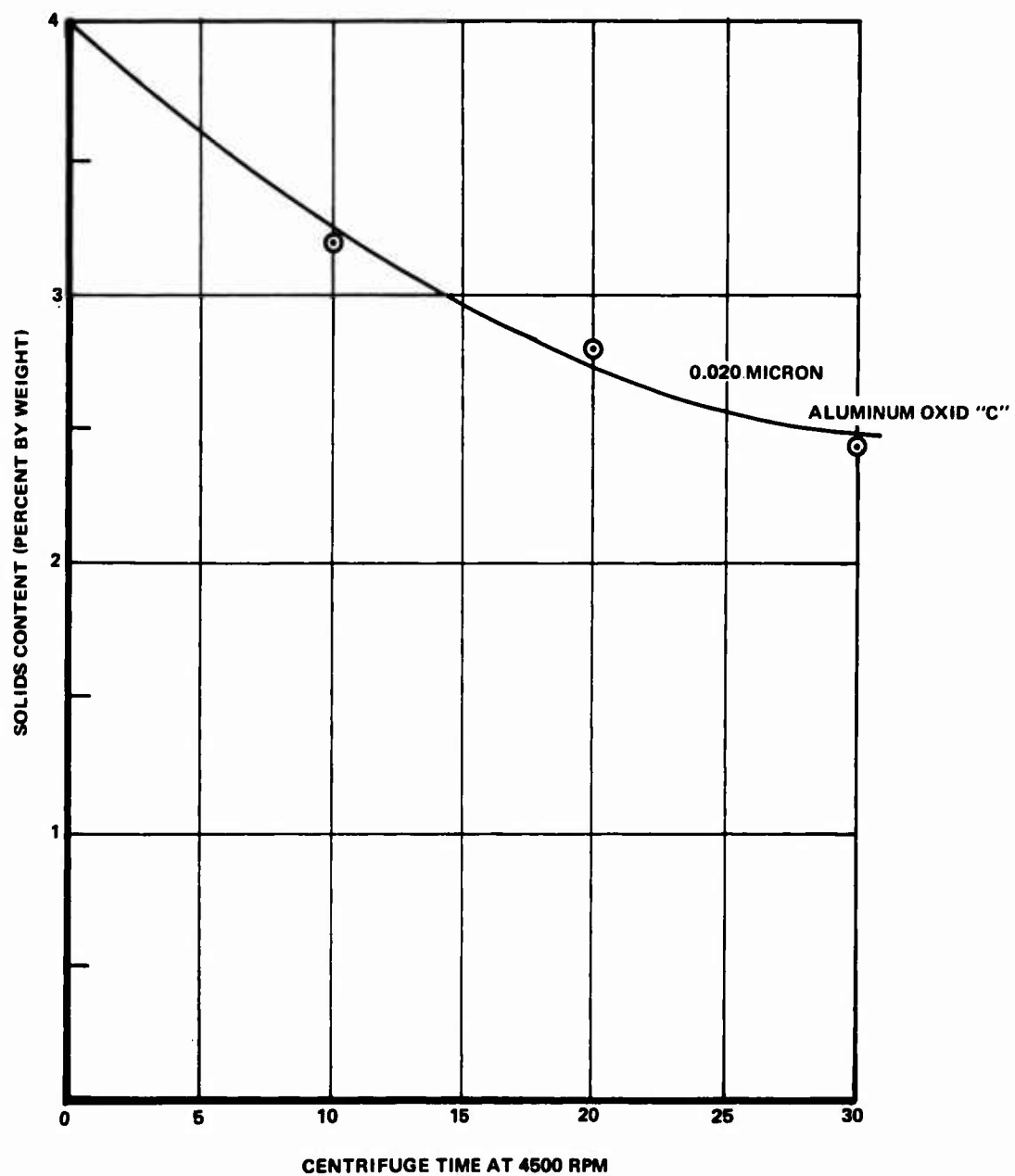
Figure 13.   Suspension Solids Content versus Centrifuge Time at 4500 RPM
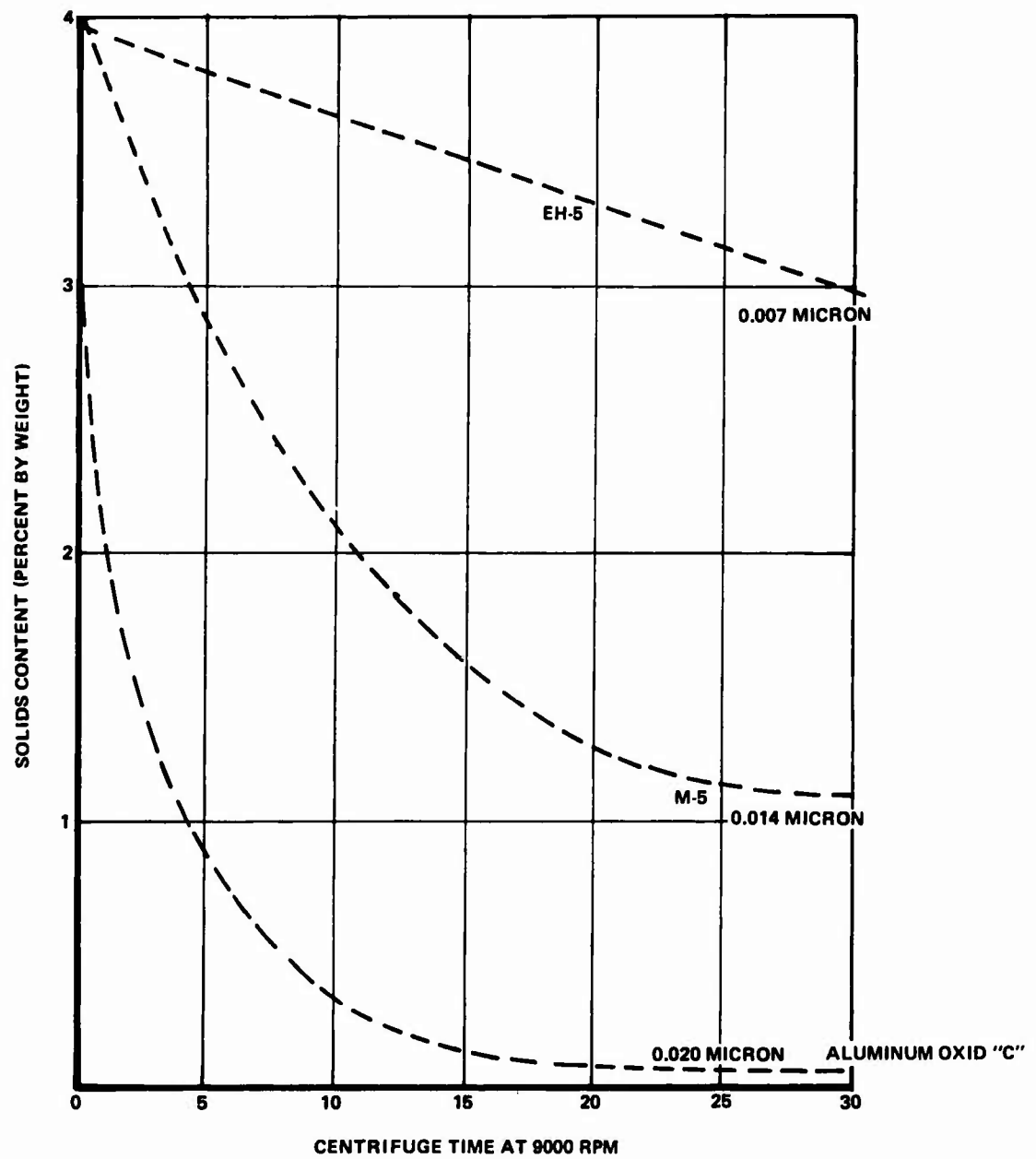
Figure 14. Suspension Solids Content versus Centrifuge Time at 9000 RPM
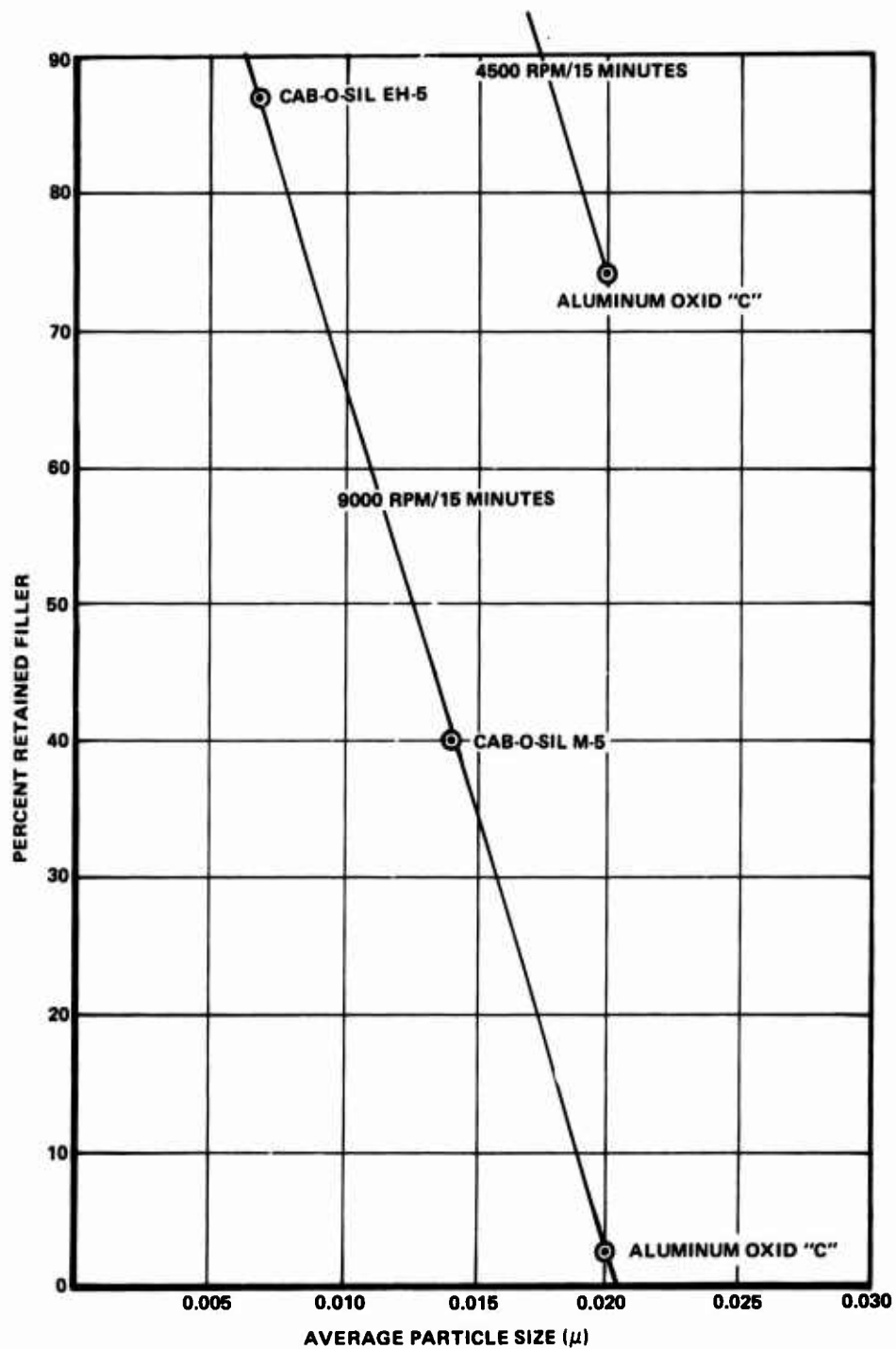
Figure 15. Percentage of Retained Filler versus Average Particle Size

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Utilizing the 4500 rpm and 9000 rpm lines and plotting a separate line of Y_I intercept versus speed (2 points), its slope may be calculated and its intercept determined from the new line. The coordinates of the two points would be (9000, 132) and (4500, 204). The slope becomes -0.016 and the intercept 270, or

$$Y_I \text{ Intercept} = -0.016R + 270 \quad ,$$

where R equals the speed/15 minutes. Substituting the Y_I intercept for b in the original equation, a new equation appears:

$$Y = -6500x - 0.016R + 270 \quad .$$

From this equation, the centrifuge speed and time can be determined for any percentage of particles desired in the remaining suspension. As an example, if it is desired to retain 50 percent of the particles in suspension after centrifuging for 15 minutes, Table 14 shows the centrifuge speeds which would be required:

$$R = \frac{-6500(x) - y + 270}{0.016} \quad .$$

where

       R = Centrifuge speed for 15-min period
    (x) = Nominal particle size
    (y) = Particle retention required (percent).

TABLE 14. CENTRIFUGE SPEED REQUIRED FOR 50-PERCENT PARTICLE RETENTION

Particle	Nominal particle size (μ)	Particle retention required (percent)	Calculated centrifuge speed over 15 min period (rpm)
Aluminum Oxid "C"	0.02	50	5,625
Cab-O-Sil M-5	0.014	50	8,063
Cab-O-Sil EH-5	0.007	50	10,906

8. OPTIMIZING COMPONENT RATIOS

The epoxy binder (XD-7080/DER 332), the polysilicic acid released from the 99-percent TEOS, and the prehydrolyzed ethyl polysilicic acids (H-4) were varied toward a single coating with an intermediate hardness, clarity, and adhesion which could be further modified toward ultimate hardness by the addition of other materials. A listing of the various unfilled formulations and their compositions by weight is shown in Table 15. Table 16 shows similar information, except a silicon dioxide of submicron sized particles has been added.

9. FURTHER MODIFICATIONS

Further modifications included the effect of cure time, the sequence of component addition, and the addition of a cross-linking agent to improve the hydrolytic stability. Infrared analytical scans of the unfilled coating variations in Table 15 indicated that:

1. A minimum of 37 hours at $+200^o$ F would be required to remove most of the water

2. A cross-linking additive would be necessary to bind the remaining water as well as the hydroxyls in the polysilicic acid and curing epoxy components.

The cross-linking material chosen (Silane A-187 ⓉⓂ) was initially balanced in varying small quantities into the basic coating formulation, without filler, to determine a range of nonhazing additions. The final proportion of Silane was obtained from plotting the haze measurements and the weight ratio of Silane to Cab-O-Sil EH-5. Haze, appearance, and hardness were qualitatively evaluated with filler on triangular coordinate charts (see Figures 16, 17, and 18). The curve in Figure 19 indicates that a ratio of approximately 1.3 pbw for 1.0 pbw of the EH-5 filler (silicone dioxide) would be optimum if haze is to be a minimum.

Figure 20 is an ATR[a] scan which represents a cure state obtained after 18 hours at $+190^o$ F. The cure is apparently practical for stretched Plex 55 coatings.

ⓉⓂ Silane A-187 - trademark of Union Carbide, Chemical and Plastics Div., New York, N.Y.

[a] ATR - Attenuated Total Reflectance (infrared).

TABLE 15. COMPOSITION BY WEIGHT OF VARIOUS UNFILLED COATING
FORMULATIONS (NONVOLATILE COMPONENTS)

Formulation no.	Epoxy binder (percent)	Polysilicic acid – A (percent)	Polysilicic acid – B (percent)
105	57. 8	25. 8	16. 4
106, 107, 108	43. 5	19. 4	37. 1
113	38. 0	24. 9	37. 1
114	43. 5	14. 9	41. 6
115	42. 9	22. 0	35. 1
116	42. 3	28. 8	28. 9
117	48. 1	18. 8	33. 1
118	38. 8	24. 6	36. 6
120	38. 4	24. 8	36. 8

TABLE 16. COMPOSITION BY WEIGHT OF VARIOUS FILLED COATING
FORMULATIONS (NONVOLATILE COMPONENTS)

Formulation no.	Cab-O-Sil EH-5 (percent)	Epoxy binder (percent)	Polysilicic acids A and B (percent)
109	0. 8	43. 1	56. 1
110	3. 7	41. 8	54. 5
111	1. 9	42. 6	55. 5
112	0. 8	43. 1	56. 1
119	9. 3	39. 0	51. 7
122	2. 6	42. 4	55. 0
123	2. 7	42. 3	55. 0
124	1. 3	42. 9	55. 8
125	0. 7	43. 2	56. 1
129	1. 2	43. 0	55. 8
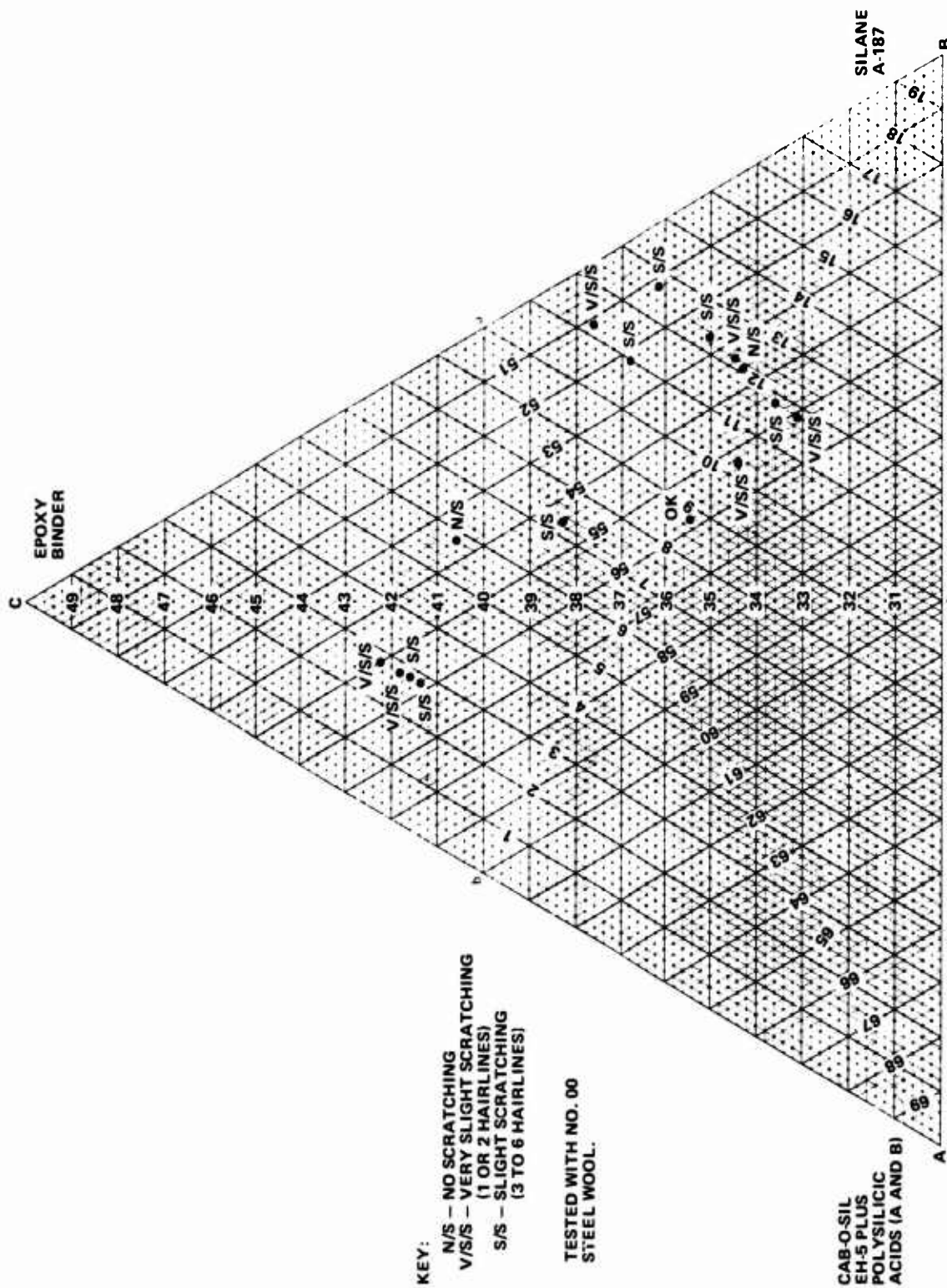
Figure 16. Hardness Comparisons
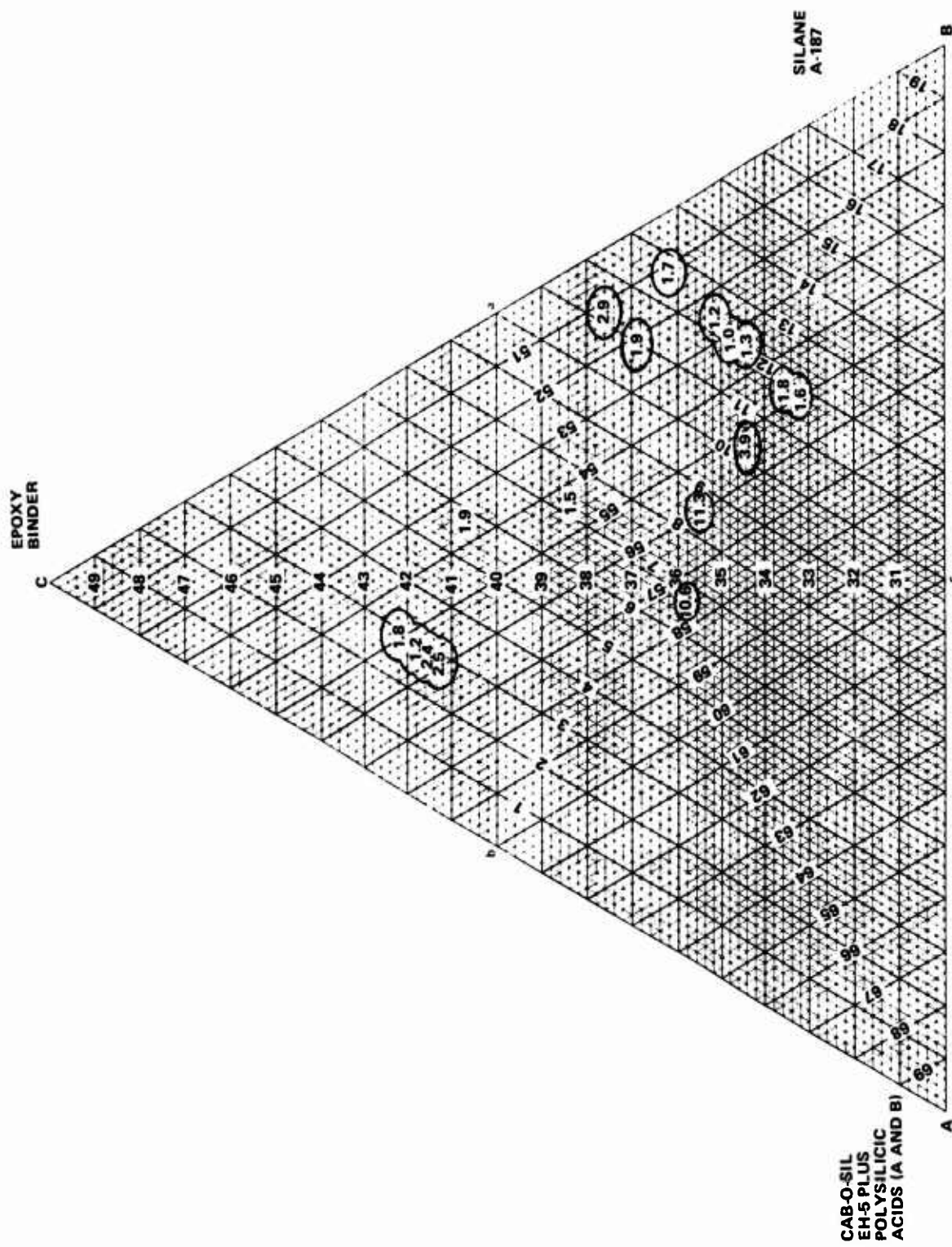
Figure 17. Percent Haze Comparisons
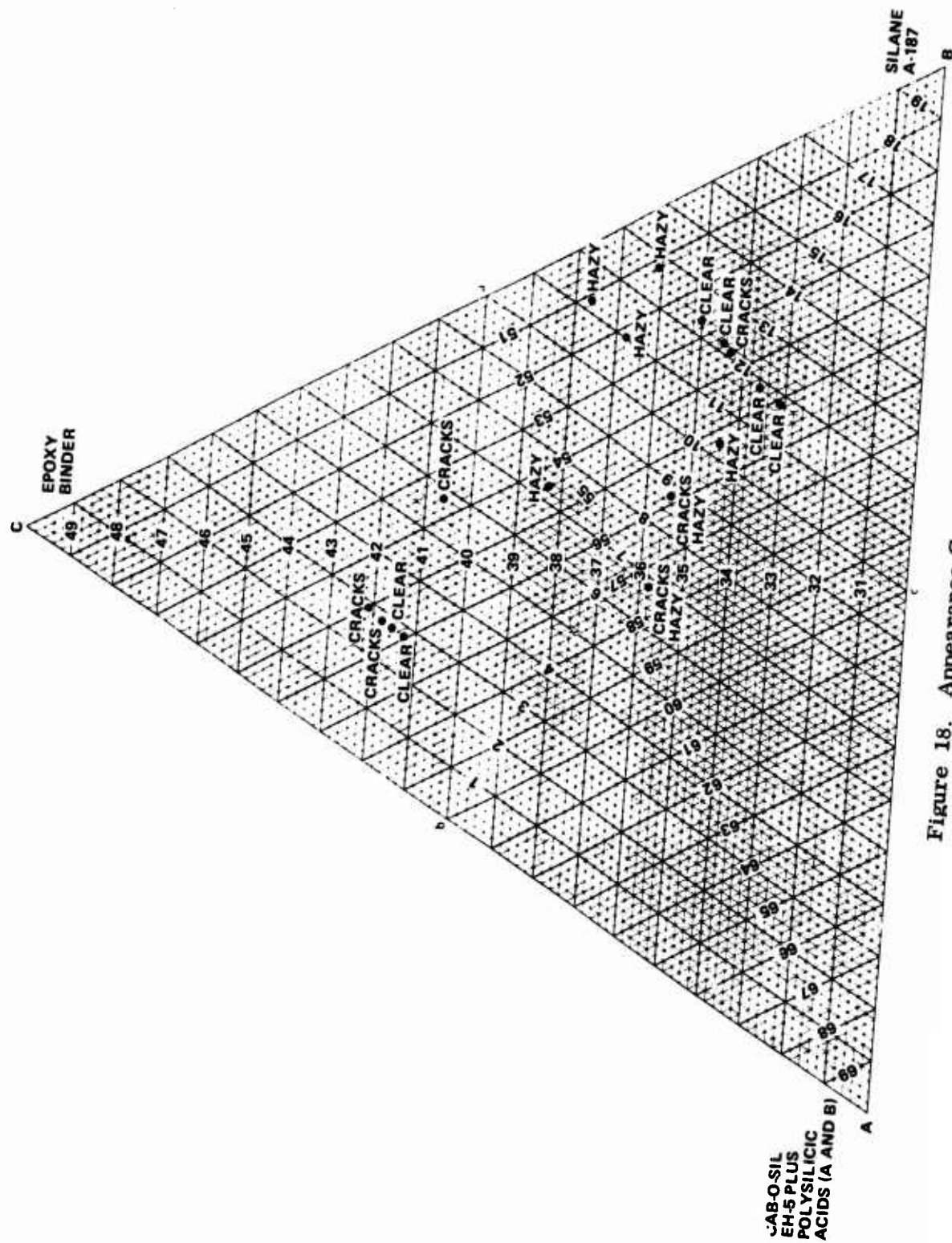
Figure 18. Appearance Comparisons
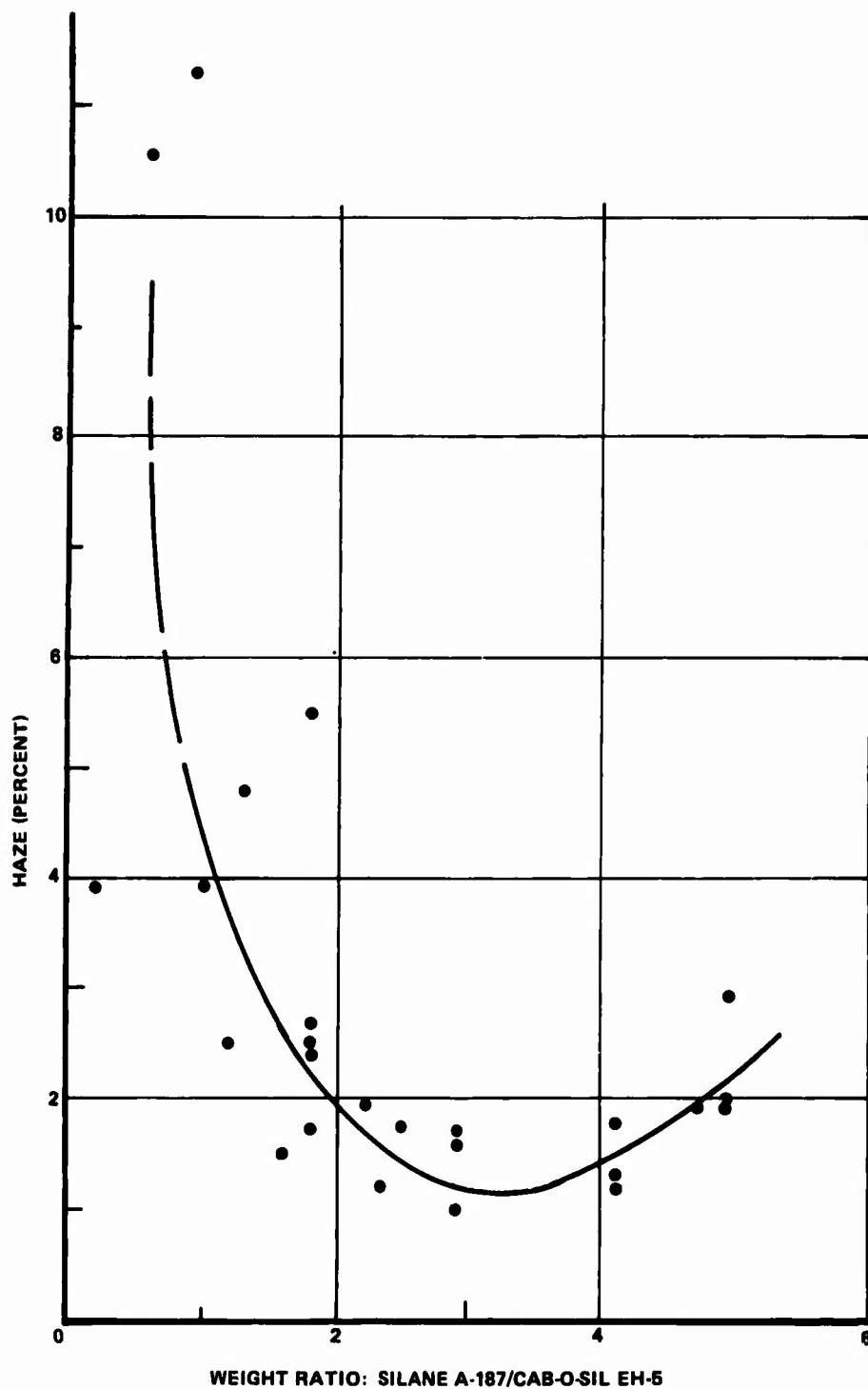
Figure 19. Weight Ratio Silane A-187/Cab-O-Sil EH-5 versus Percent Haze

INFRARED SCANS (MULTIPLE INTERNAL REFLECTION ACCESSORY,
INTERNAL ANGLE OF INCIDENCE: 30 DEG)

FREQUENCY (CM^{-1})

AFTER CURE
(18 HOURS AT 170° F)

3650-3200   -OH STRETCH
3000-2800   C-H ALIPHATIC
3000-2700   -CH$_2$- STRETCH

BEFORE CURE
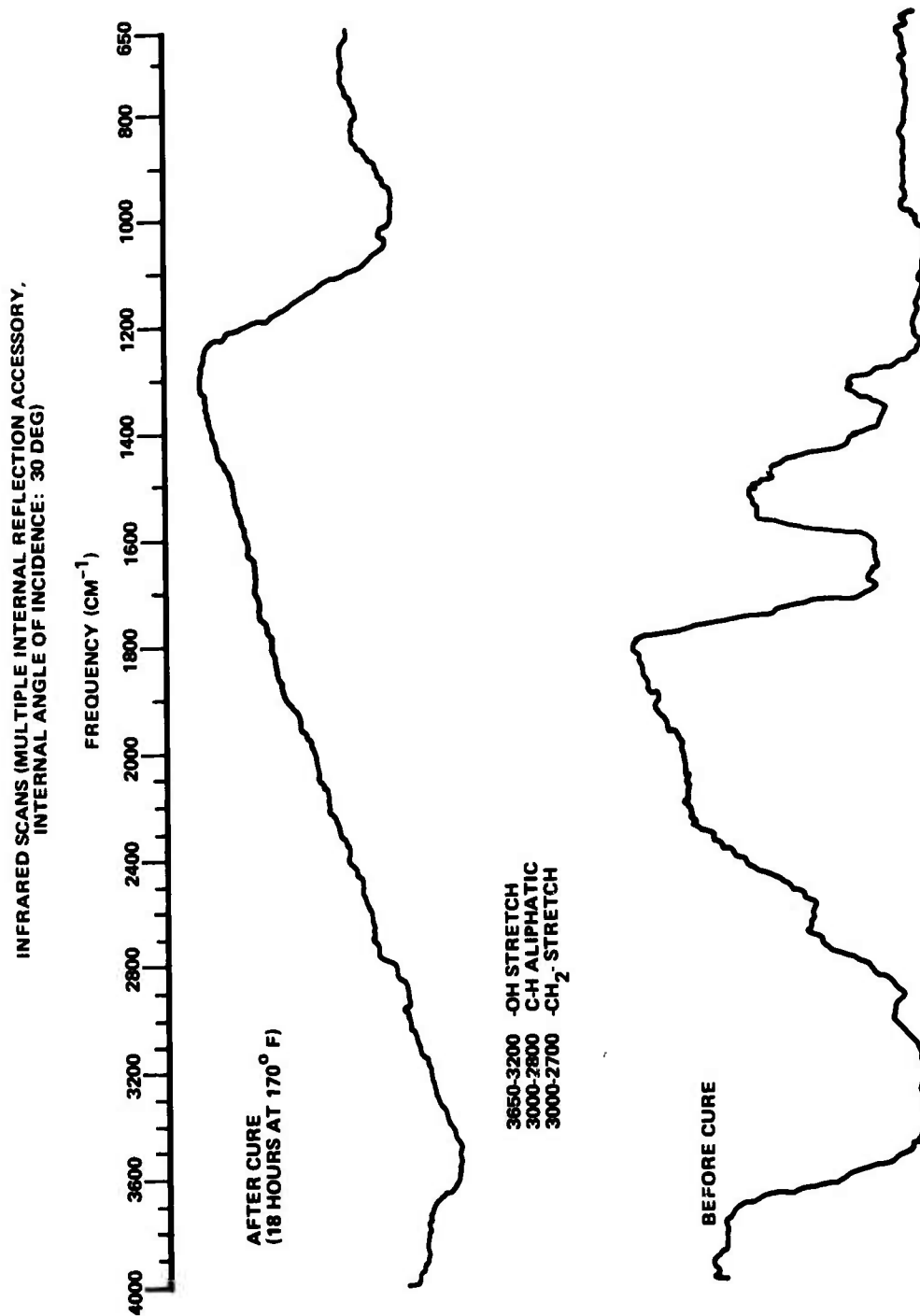
Figure 20.   Infrared Coating Cure Profile

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Variances in coating hardness over a surface from the top to the bottom of a pour indicated an inconsistency in coating thickness. In an attempt to decrease viscosity, a quantity of ethanol was added which provided a more consistent coating although some loss in hardness was apparent. It was also postulated that a thinner coating would be less likely to crack from substrate expansion.

10. SCREENING

Panel coating formulations 183 through 214 were prepared and screened into three formulations. The basic differences were:

1. No. 188 - contained no filler

2. No. 210 - contained 3.29 percent of EH-5 silicone dioxide filler

3. No. 214 - contained 1.69 percent of Aluminum Oxid "C".

The latter is presumably a competitive material to Alon and is manufactured by Degussa Inc.

Screening was accomplished through hardness tests with No. 00 steel wool, light transmission and haze tests, adhesion results, and general appearance. Most of the work with these formulations was performed on unprimed stretched Plex 55 without any adhesion problems under normal conditions and preliminary humidity testing.

The basic coating system did not adhere well to polycarbonate and as-cast acrylic. The decision was made to proceed with the three choices on stretched Plex 55 to complete the program with the option of modification or primer development at a later time for adherence to other substrates.

The light transmission and haze measurements are given in Table 17.

All passed the hardness test with No. 00 steel wool and the No. 250 tape adhesion test. The stretched Plex 55 substrates were a nominal 0.100 in. thick.

The various fillers which have been considered are listed in Appendix B with their properties.

TABLE 17.   LIGHT TRANSMISSION AND HAZE MEASUREMENTS BEFORE AND
AFTER COATING

Formulation	Filler	Trade identification	Before coating		After coating	
			Light transmission	Haze	Light transmission	Haze
188	None	–	92.2 %	1.6 %	92.2 %	1.2 %
210	SiO_2	EH-5	92.1	1.9	91.9	1.4
214	Al_2O_3	Al Oxid "C"	92.0	1.4	91.8	2.5

Electron microphotographs of the three surfaces are shown in Figure 21.   The
No. 188 coating exhibits a finer irregularity, and has smaller imperfections
than the filled coatings.   It is interesting to note the relative sizes of the individual
filler particles are in the submicron range, but the agglomerates tend to be larger
despite refinement measures.   The greater number of holes and/or pits in the filled
materials may result in a lesser degree of hydrolytic stability than the unfilled
material.

(A) NO. 188 FORMULATION (NO FILLER)

(B) NO. 210 FORMULATION (SiO$_2$ FILLER)
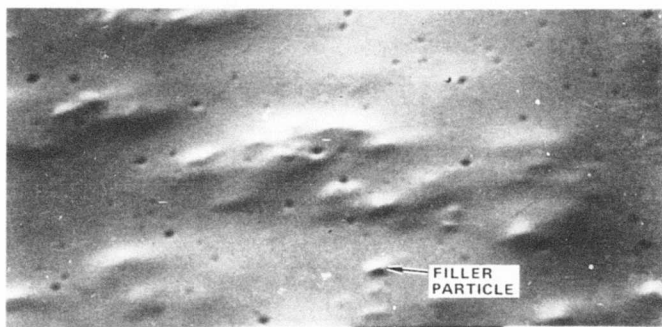
(C) NO. 214 FORMULATION Al$_2$O$_3$ FILLER

Figure 21. Electron Microphotographs of Filled and Unfilled Transparent Hard Coatings on Stretched Plex 55 Substrate (Black Marker Represents 4 Microns of Length)

SECTION IX

TESTING

1. TEST PLAN

The test plan, approved earlier in the program, was based on testing a single
coating formulation which had been applied to three different substrates. The
test schedule is shown in Table 18. Because the newly developed coating system
was only compatible with the stretched Plex 55, the program was altered by
testing three variations of the system on a single substrate.

2. TEST RESULTS

a. Outdoor Weathering

The results of testing on specimens weathered for 36 days in Arizona are
shown in Table 19.

b. Artificial Weathering (Weather-O-Meter)

Artificial weathering was accomplished with 1-in. strips of aluminum foil
shielding the substrate. One strip was removed every 100 hours. Table 20
provides the 100-hour increments of light transmission and haze values with
the overall results of the other test methods. Figure 22 plots the haze values
in 100-hour increments.

c. Artificial Weathering (Ultraviolet Exposure)

Ultraviolet exposure was accomplished without the presence of moisture. The
relative increase in the percentage of haze after 36 days is shown in Figure
23. No appreciable change was noted in the other properties.

d. Humidity Exposure

(1) Constant Humidity Exposure

Constant humidity of 95 percent was maintained at $+120^{\circ}$ F for 10 days.
The exposed specimens were then exposed to two severe modes of
abrasion through the use of a reciprocating arm abrader (to represent
windshield wiper action) and a salt abrader (to represent ice particle
or dust impingement). The former was subjected to 3000 cycles (wet)

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TABLE 18. TEST SCHEDULE

Test sequence	Conditioning	Tests	Applicable specifications	Variations	Data	Remarks
I. Weathering (6 panels)	Natural weathering Accelerated weathering Ultraviolet exposure	Light transmission Haze Adhesion Hardness Visual	FTMS-406-3022 FTMS-406-6024 ASTM-G-26-70 GAC-CLA-12799 A ASTM-D-1435	Moisture not included in FTMS-406-6024	Percent transmission (before - after) Percent haze (before - after) Percent adhesion, Procedure "A" (before - after) Go-no go adhesion, Procedure "B" (250 tape) before - after Approximate hardness - Mohs scale (before - after) Description of failure	
II. Humidity and abrasion (18 panels)	Constant humidity exposure Cycled humidity exposure Ambient abrasion exposure (salt impingement and reciprocating arm)	Haze Adhesion Hardness Visual Color	FTMS-406-3022 MIL-STD-810C-507 JAN-H-792 GAC-CLA-4038 GAC-CLA-12800 A ASTM-D-1544 GAC-CLA-12799 A GAC-CLA-4099 GAC-CLA-4098	Liquid to solid color comparison made in ASTM-D-1544 "After" tests to be performed 12 hours after specimens are removed from humidity chambers	Percent haze (before and after humidity) Percent haze (before and after abrasion) Go-no go adhesion, Procedure "B" (250 tape) (before and after humidity) Approximate hardness - Mohs scale (before and after humidity) Description of failure Color no.	Periodic visual examination and adhesion testing to be performed during humidity cycling Optical properties are included in these tests
III. Solvent resistance (3 panels)	Exposure (15 minutes) to 10 solvents Ambient abrasion exposure (salt impingement)	Haze Adhesion Hardness Visual	GAC-CLA-4038 GAC-CLA-12799 A FTMS-406-3022 GAC-CLA-4099 GAC-CLA-4098		Percent haze (before and after solvent attack) Go-no go adhesion, Procedure "B" (250 tape) (before and after solvent attack) Approximate hardness - Mohs scale (before and after attack) Description of failure	

Note: All panels from which specimens are cut are 12 in. × 12 in.

TABLE 18. TEST SCHEDULE (CONT)

Test sequence	Conditioning	Tests	Applicable specifications	Variations	Data	Remarks
IV. Ductility (12 panels)	Specimens soaked at -65, 0, room temperature, +120, and +165 deg F for low impact test	Low impact energy High impact energy Mandrel ductility Visual	GAC-CLA-2326 GAC-CLA-12798A GAC-CLA-4100		Height at which coating fracture occurs Weight of dart or plummet Temperature of specimen Description of coating fracture Radius of mandrels Calculated elongation of coating	Coating side should be exposed to the strike
V. Thermal resistance (15 panels)	Thermal shock Specimens abraded at -65, 0, +120, and +165 deg F with reciprocating arm abrader	Visual haze	MIL-STD-810C-503 GAC-CLA-12800A FTMS-406-3022	Reciprocating arm abrader to be used dry	Description of coating failure, if any Percent haze increase Temperature of specimens	Because of low temperature requirements, reciprocating arm abrader will be run dry for all temperatures. Data will not be comparable to data obtained by the wet process
VI. Mechanical (6 panels)	Section 4, paragraph 4.3 of FTMS-406	Tensile strength Flexural strength Bearing strength	FTMS-406-1011 FTMS-406-1021 FTMS-406-1051		Standard	Tests to be performed on coated and uncoated specimens to determine any change in strength because of coating process

Note: All panels from which specimens are cut are 12 in. × 12 in.

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TABLE 19. OUTDOOR WEATHERING (36 DAYS)

Formulation	No. 188	No. 210	No. 214
Original light transmission (%)	91.9	91.5	91.1
After 50 days	91.7	91.5	90.9
Change	-0.2	-0-	-0.2
Original haze (%)	1.4	2.2	5.0
After 50 days	3.5	3.4	3.8 to 5.4
Change	+2.1	+1.2	-1.2 to +0.4
Hardness (Mohs')	>5.0	=5.0	=5.0
After 50 days	-	-	-
Change	-	-	-
Appearance	Clear, no cracks	Clear, no cracks	Slight haze, no cracks
After 50 days	-	-	-
Change	-	-	-
Adhesion (%)	100	100	100
After 50 days	100	100	100
Change	None	None	None

TABLE 20. ARTIFICIAL WEATHERING – ASTM-G-26-70 (500 HOURS)

Formulation	No. 188	No. 210	No. 214
Original light transmission and haze (%)	91.7/3.3	91.1/3.2	91.0/6.8
After 100 hours	92.0/5.0	91.8/3.7	91.7/5.0
After 200 hours	91.1/13.8	91.7/3.2	91.6/4.8
After 300 hours	91.4/8.0	91.4/5.7	91.4/6.5
After 400 hours	91.6/3.7	91.4/4.2	90.6/10.6
After 500 hours	91.6/3.2	91.4/3.2	90.6/10.4
Hardness			
After 500 hours	–	–	–
Change	–	–	–
Appearance			
After 500 hours	Aluminum oxide staining*	Aluminum oxide staining*	Aluminum oxide staining*
Change	–	–	–
Adhesion			
After 500 hours	–	–	–
Change	–	–	–

*A nonhomogeneous cloudiness from surface stains occurred which could not be completely removed by superficial cleaning methods.
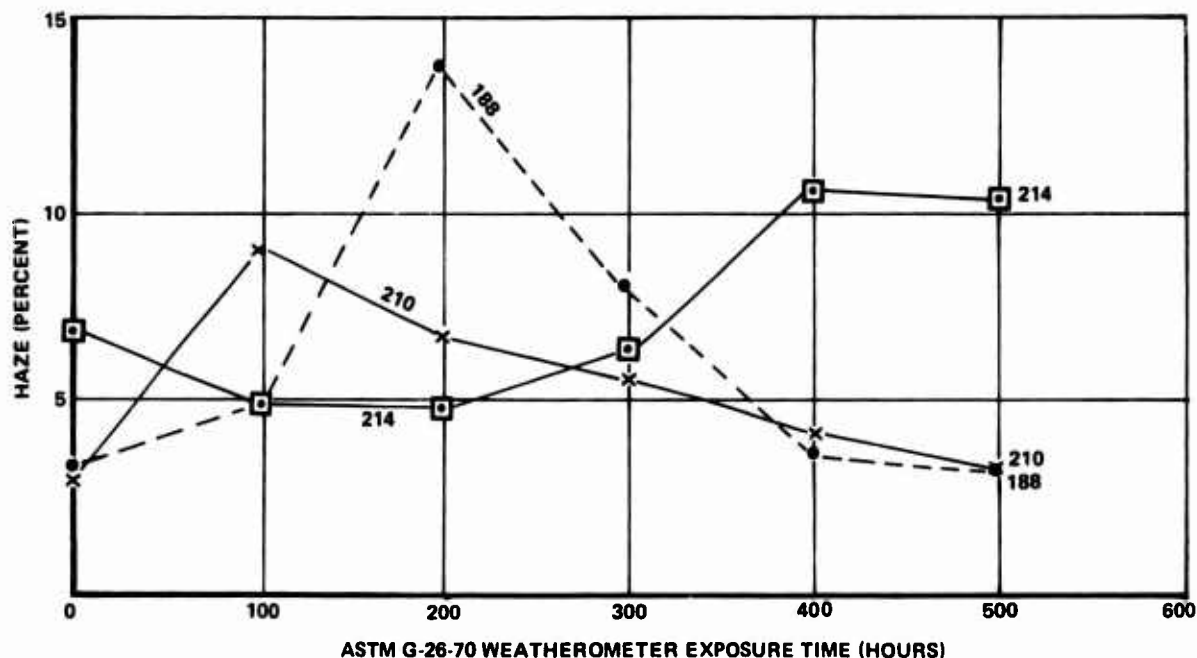
Figure 22. Artificial Weathering of Three GAC Formulations - Percent Haze versus Exposure

with no appreciable change in haze measurements (see Figure 24). The latter was run beyond coating breakthrough which occurred in fewer than 100 cycles (see Figure 25).

For further analysis of the results shown in Figure 25, the coating thicknesses were determined through edge measurements using a scanning electron microscope and photographic technique. The coating thicknesses were as shown in Table 21. Erosion rates were obtained by establishing the number of cycles of salt abrasion for coating breakthrough divided by the film thickness for both unexposed and exposed specimens to humidity conditions. These in turn were placed in a rank analysis based on 156.3 ranking as 10. These variations are shown in Table 22.
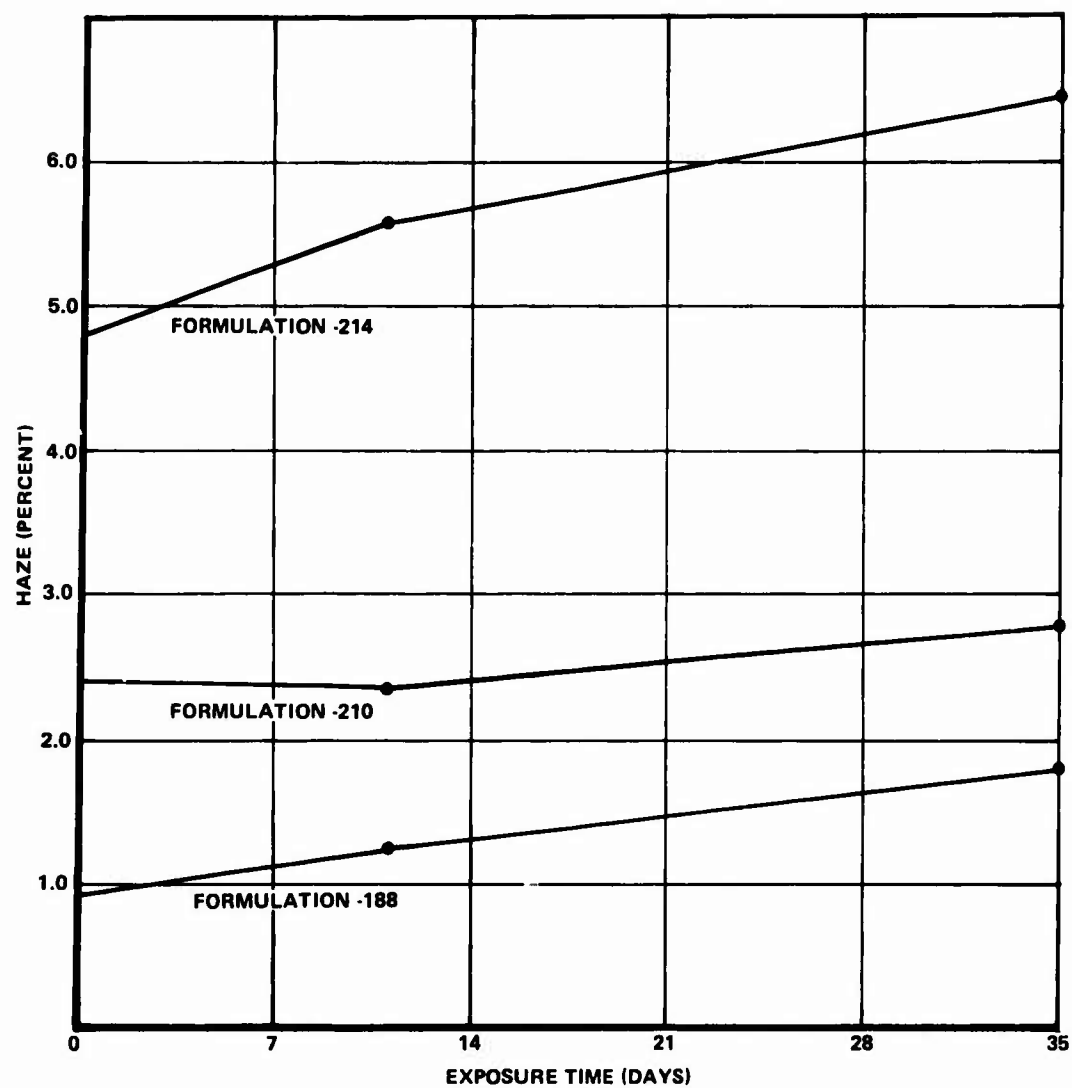
Figure 23.   Artificial Weathering - Ultraviolet Exposure

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FORMULATION	PERCENT HAZE AFTER RECIPROCATING ARM ABRADER CYCLES					
	500	1000	1500	2000	2500	3000
188	2.1	1.9	2.1	2.4	2.8	2.4
210	3.8	3.2	3.6	3.1	3.2	3.3
214	6.1	5.6	5.3	5.8	5.2	5.9

CONDITIONS: MIL-STD-810C, METHOD 507.1, PROCEDURE I
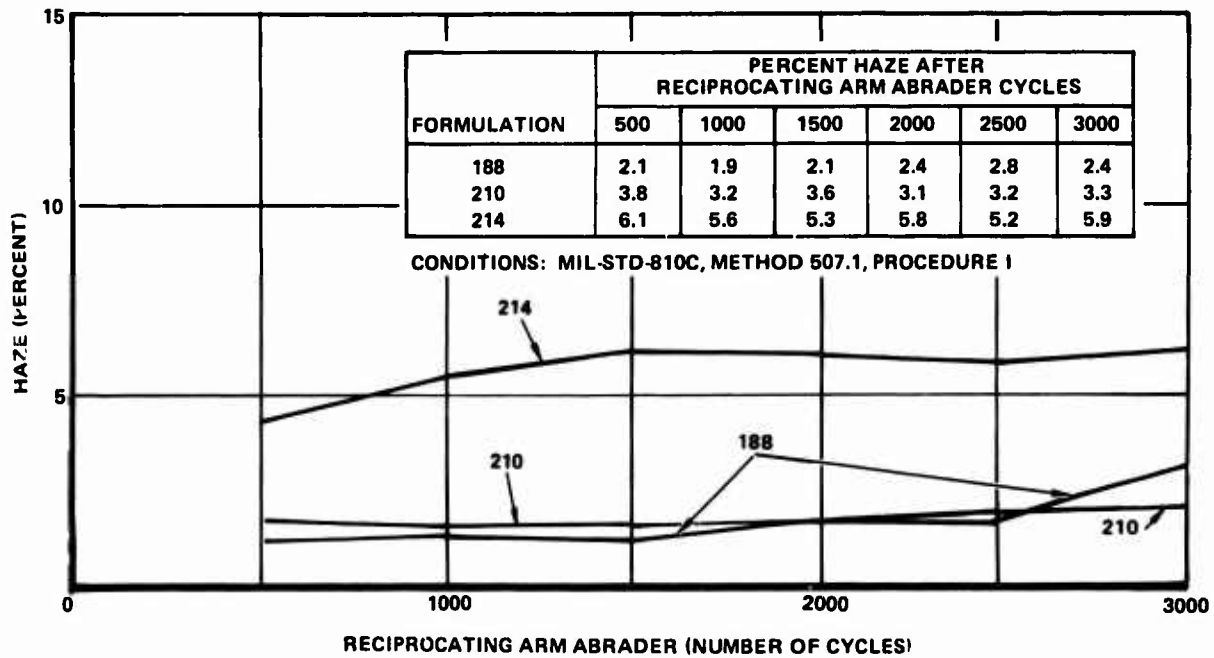
Figure 24. Haze versus Cycles of Reciprocating Arm Abrader after Constant Humidity Exposure (10 Days)

(2) Cyclic Humidity Exposure

Cyclic humidity exposure was performed in accordance with MIL-STD-810C, Method 507.1, Procedure I. The two methods of abrasion testing were again used with the results shown in Figures 26 and 27.

(3) Salt Abrasion Tests on Control Specimens

Figure 28 demonstrates the effect of salt abrasion on coated specimens which have not been environmentally exposed.

e. Solvent Resistance

The solvent resistance test was to simulate accidental exposure of solvents on coated transparencies followed by subjection to dust or ice particle impingement through the salt impingement test.
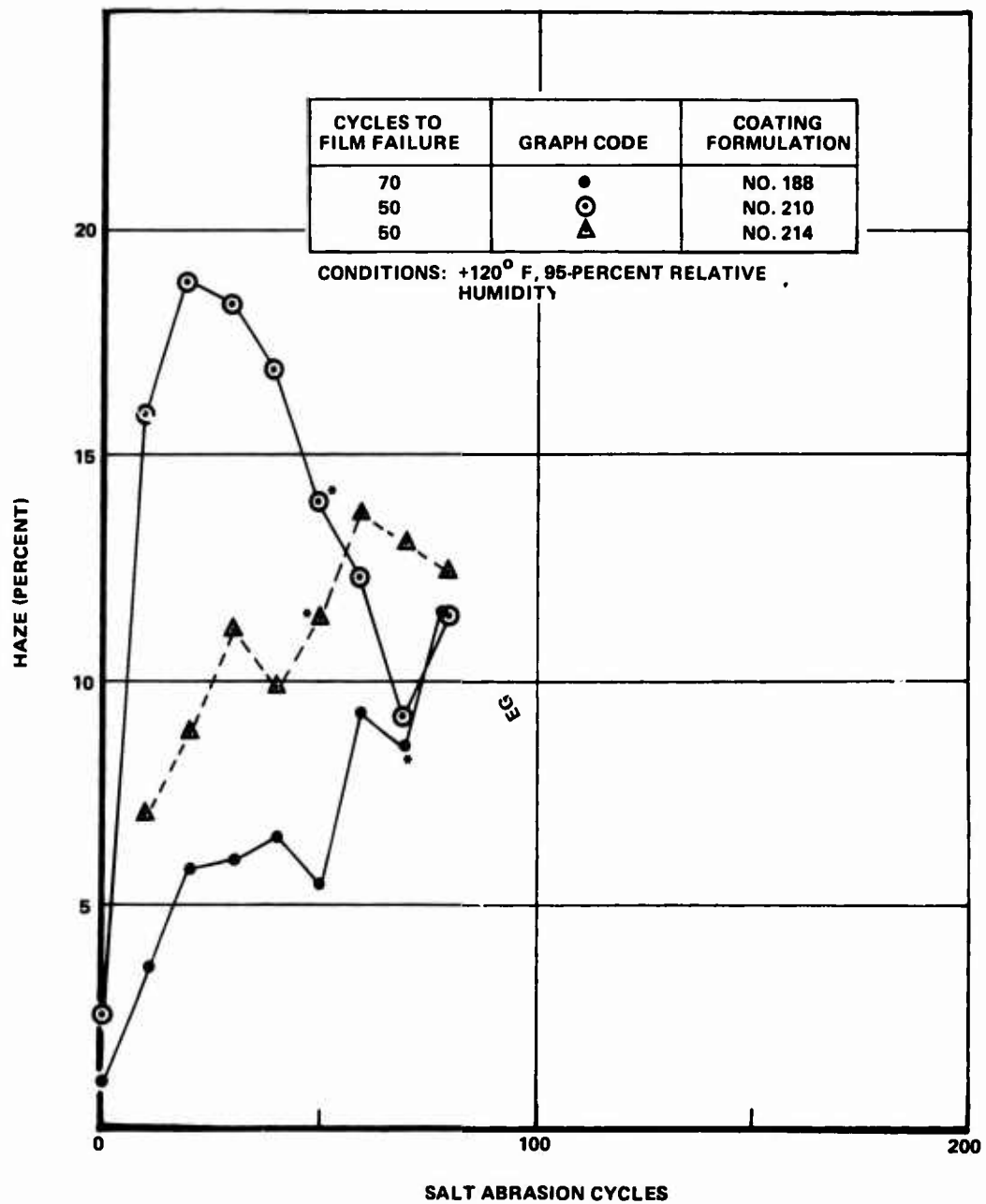
Figure 25. Percent Haze versus Cycles of Salt Abrader after Constant Humidity Exposure (10 Days)

TABLE 21. FILM THICKNESS MEASUREMENTS (MICRONS) -
SCANNING ELECTRON MICROSCOPE TECHNIQUE

System	Control	Condition - A, constant humidity	Condition - B, cyclic humidity/temperature exposure
GAC-188	3.2μ	3.59μ	1.36μ
GAC-210	1.6μ	1.58μ	4.85μ
GAC-214	2.0μ	3.24μ	2.05μ

TABLE 22. EROSION RATES AND RANK ANALYSIS OF COATINGS PREVIOUSLY
SUBJECTED TO HUMIDITY CONDITIONS

	Control	Condition - A, constant humidity exposure	Condition - B, cyclic humidity/temperature exposure
Erosion Rates			
GAC-188	15.6	19.5	36.8
GAC-210	156.3	31.6	66.0
GAC-214	65.0	15.4	39.0
Rank analysis			
GAC-188	1	1	2
GAC-210	10	2	4
GAC-214	4	1	2

Notes:

1. Color change was not appreciable and not measurable according to Gardner standard.

2. Erosion rates = salt abrasion cycles/μ at breakthrough.

| FORMULATION | PERCENT HAZE AFTER RECIPROCATING ARM ABRADER CYCLES | | | | | |
	500	1000	1500	2000	2500	3000
188	1.2	1.3	1.2	1.7	1.7	3.1
210	1.7	1.6	1.7	1.7	1.9	2.1
214	4.3	5.6	6.1	6.0	5.8	6.1

CONDITIONS: +120° F, 95 PERCENT RELATIVE HUMIDITY
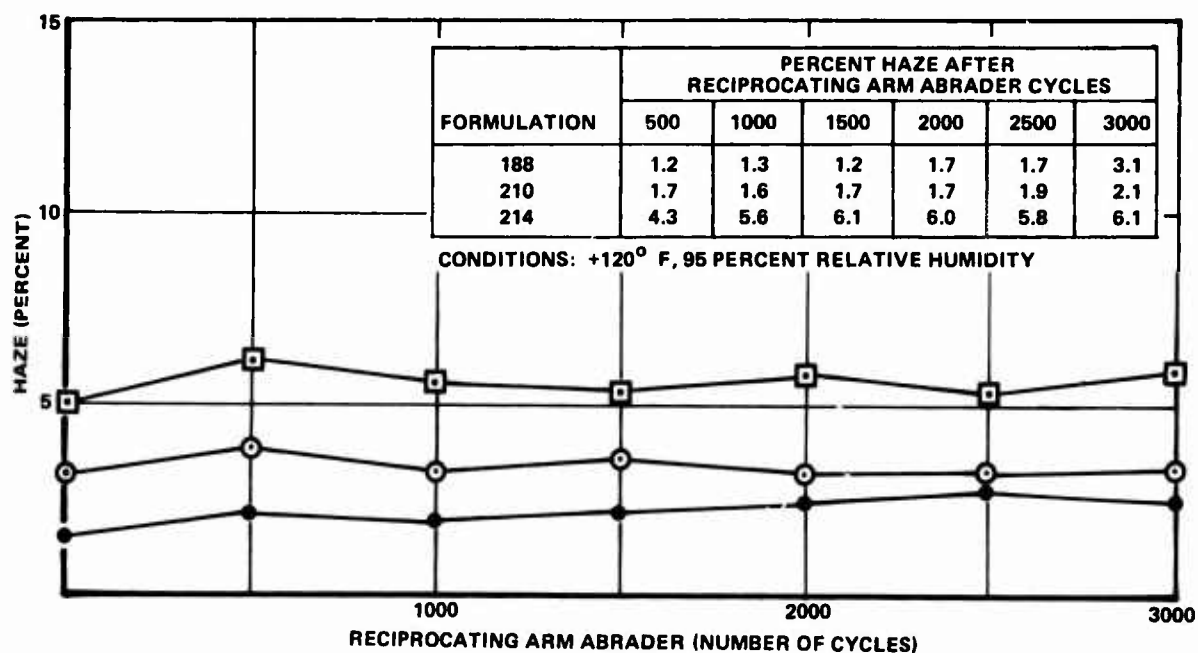
Figure 26. Percent Haze versus Cycles of Reciprocating Arm Abrader after Cyclic Humidity Exposure

The abrasion was limited to a constant of 50 cycles with haze measurements used as the criteria. Referring to Tables 23, 24, and 25, an original haze measurement was made on each specimen prior to subjection to 50 cycles of the salt abrader. A second haze measurement was made on each specimen and the amount of haze change   recorded. This provided a haze change caused only by abrasion. The salt abraded area and an adjacent area were then exposed to one different solvent for each specimen for 15 minutes. A third haze measurement in the solvent-attacked, but unabraded, area showed the change caused only by solvent attack. The last haze measurement showed the result of abrasion on an area which had been solvent attacked.

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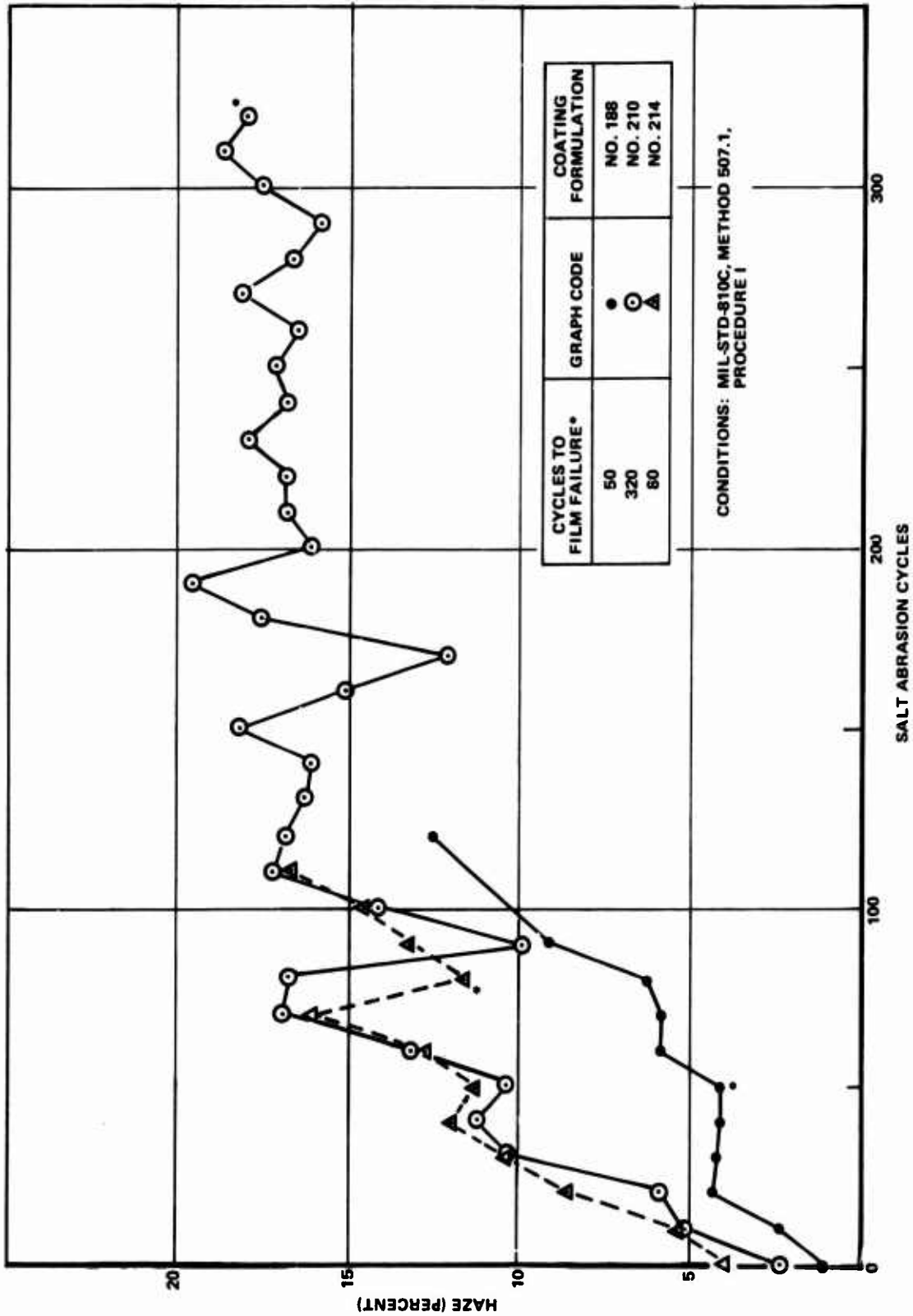
Figure 27.   Percent Haze versus Cycles of Salt Abrader after Cyclic Humidity Exposure (10 Days)
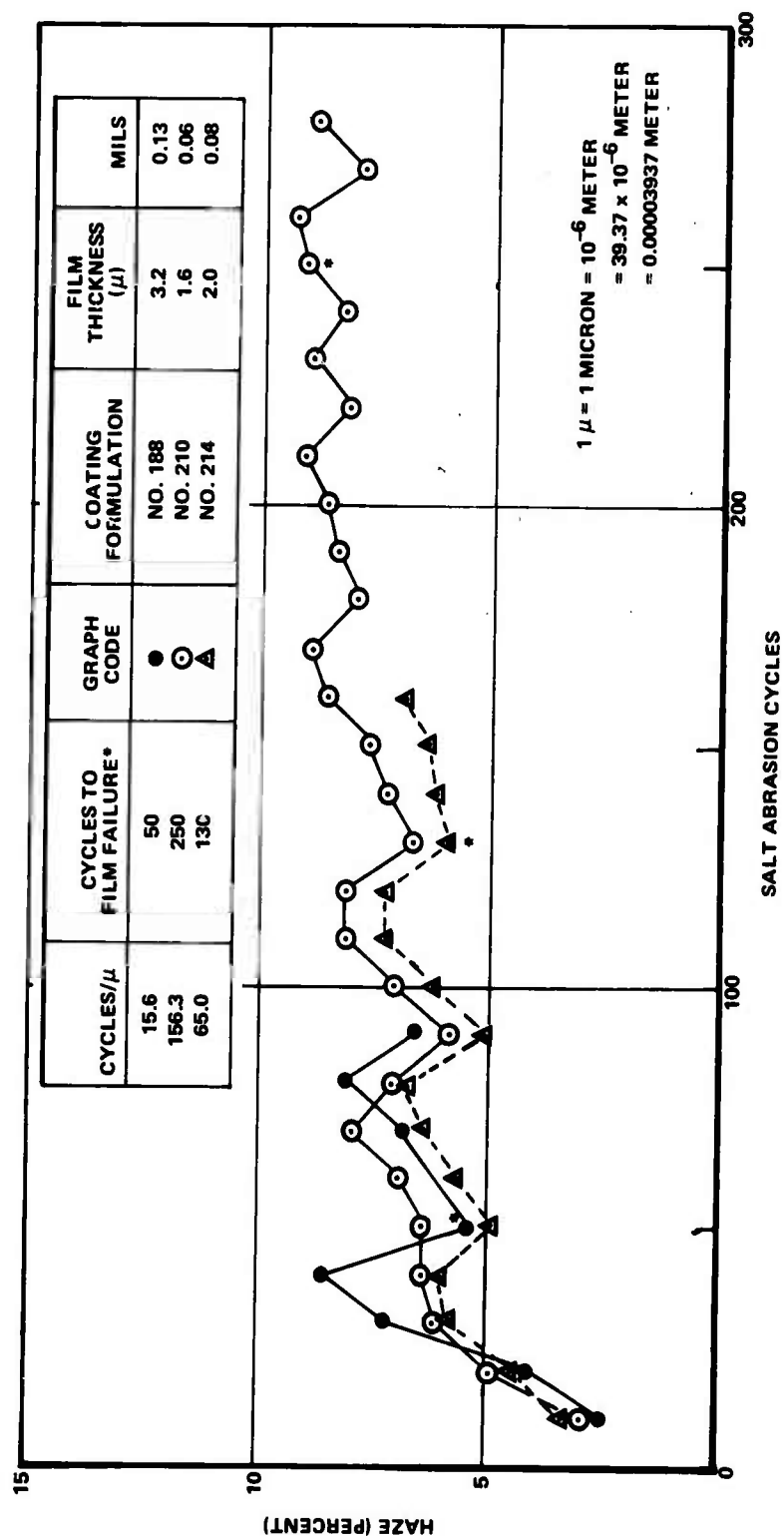
Figure 28. Cycled Salt Abrasion Controls (Room Temperature Environment Only)

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TABLE 23. SOLVENT RESISTANCE TEST - FORMULATION NO. 188 (NO FILLER)

	MEK	Acetone	MIBK	Toluene	Hexane	Butyl alcohol	Methyl alcohol	Lacquer thinner	Isopropyl alcohol	Xylene	Maximum haze increase allowed
First haze measurement 1	0.8	2.2	0.7	1.2	4.1	1.4	0.8	0.7	1.4	1.5	-
Second haze measurement* 2	2.9	5.4	3.8	6.1	8.8	3.1	3.2	4.0	3.4	3.3	-
Δ percent haze 2 - 1 =	2.1	3.2	3.1	4.9	4.7	1.7	2.4	3.3	2.0	1.8	<3
Third haze measurement 3	1.6	1.8	1.3	1.5	1.4	0.9	1.4	1.3	1.0	-	-
Δ percent haze 3 - 1 =	0.8	-0.4	0.6	0.3	-2.7	-0.5	0.6	0.6	-0.4	-	-
Fourth haze measurement* 4	8.8	9.0	2.7	4.9	5.0	5.7	3.6	2.8	3.1	-	-
Δ percent haze 4 - 3 =	7.2	7.2	1.4	3.4	3.6	4.8	2.2	1.5	2.1	-	-

Note: Δ = change.

*After 50 cycles (salt abrader).

TABLE 24. SOLVENT RESISTANCE TEST – FORMULATION NO. 210 (SILICA)

	MEK	Acetone	MIBK	Toluene	Hexane	Butyl alcohol	Methyl alcohol	Lacquer thinner	Isopropyl alcohol	Xylene	Maximum haze increase allowed
First haze measurement 1	1.9	2.5	3.5	2.3	1.4	1.8	1.6	1.9	1.8	1.4	-
Second haze measurement* 2	4.0	5.3	5.6	7.6	6.4	6.9	5.2	6.9	5.7	3.5	-
Δ percent haze 2 - 1 =	2.1	2.8	2.1	5.3	5.0	5.1	3.6	5.0	3.9	2.1	< 3
Third haze measurement 3	1.9	1.7	3.1	2.1	2.9	2.0	1.8	2.1	1.9	-	-
Δ percent haze 3 - 1 =	0	-0.8	-0.4	-0.2	1.5	0.2	0.2	0.2	0.1	-	-
Fourth haze measurement* 4	2.4	6.7	6.3	6.8	7.4	6.7	6.4	4.9	5.0	-	-
Δ percent haze 4 - 3 =	0.5	5.0	3.2	4.7	4.5	4.7	4.6	2.8	3.1	-	-

Note: Δ = change.

*After 50 cycles (salt abrader).

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TABLE 25. SOLVENT RESISTANCE TEST - FORMULATION NO. 214 (ALUMINA)

	MEK	Acetone	MIBK	Toluene	Hexane	Butyl alcohol	Methyl alcohol	Lacquer thinner	Isopropyl alcohol	Xylene	Maximum haze increase allowed
First haze measurement 1	3.9	5.1	4.0	4.3	5.4	4.7	4.7	4.4	3.3	3.6	-
Second haze measurement* 2 (without solvent attack)	5.9	6.2	4.9	6.1	7.0	7.7	8.6	6.4	5.5	6.4	-
Δ percent haze 2 - 1 =	2.0	1.1	0.9	1.8	1.6	3.0	3.9	2.0	2.2	2.8	.3
Third haze measurement 3 (in unabraded area after solvent attack)	5.6	3.6	4.4	4.4	3.9	4.1	4.4	2.5	3.0	-	-
Δ percent haze 3 - 1 =	1.7	-1.5	0.4	0.1	-1.5	-0.6	-0.3	-1.9	-0.3	-	-
Fourth haze measurement* 4 (in abraded area after solvent attack)	13.6	8.0	5.8	6.4	5.0	8.2	6.3	4.8	4.7	-	-
Δ percent haze 4 - 3 =	9.0	4.4	1.4	2.0	1.1	4.1	1.9	2.3	1.7	-	-

Note: Δ = change.

*After 50 cycles (salt abrader).

f.   Ductility

Three tests were involved for ductility. Two were devised to find the amount of energy required to crack the coating. The third was a measure of the amount of flexing the coating could stand during installation or forming. The low energy 6-lb dart tests attempted on the 0.100-in.-thick specimens at room temperature were not conclusive, regardless of coating orientation. The specimen shattered prior to any evidence of coating fracture at low energy levels. The remaining low and high energy tests were cancelled. The mandrel test was performed at room temperature on the smallest required mandrel (11-in. radius). No failure occurred. A smaller 5-1/2-in. radius mandrel was procured. The coating did not fracture. The remaining, less severe 30, 42, and 49-in.-radius mandrels were not used.

g.   Thermal Resistance

This test required that the reciprocating arm abrader be used in a dry state. In testing the first specimens at room temperature, less than 500 cycles were required to gouge the specimens from an uncontrollable grit buildup and balling of the abrasion material. The test was aborted because of unpredictable data when run in a dry state (3000 cycles have been performed successfully in the wet state).

h.   Mechanical Tests

The mechanical tests were performed on an Instron Testing Instrument. The tests were to determine if the coating had any effect on the mechanical properties of the substrate. Results of tensile, flexural, and bearing tests are shown in Table 26.

TABLE 26. SUMMARY OF TESTS FOR MECHANICAL PROPERTIES ON COATED
STRETCHED PLEX 55 AT ROOM TEMPERATURE

Test	Control strength (psi)	No. 188		No. 210		No. 214	
		Strength (psi)	Variation (percent)	Strength (psi)	Variation (percent)	Strength (psi)	Variation (percent)
Tensile ultimate FTMS-406-1011	11,333	12,667	+11.8	12,264	+8.2	12,695	+12.0
Flexural yield FTMS-406-1031	21,000	20,173	-3.9	20,337	-3.2	21,475	+2.3
Bearing FTMS-406-1051	12,117	13,339	+10.1	13,712	+13.2	11,760	-2.9

SECTION X

TEST ANALYSIS

1. NATURE OF TEST

The testing, in accordance with the schedule in Table 18, was very severe in that most testing was performed after the coatings had been subjected to extended or multiple destructive environments.

2. OUTDOOR WEATHERING (36 DAYS)

The 214 formulation showed the least increase in haze but had a higher haze content to start with. No. 210 had less haze increase (1.2 percent) than the No. 188. The No. 188 showed a Mohs' hardness of less than 5 and No. 210 had an estimated hardness of 5. None were cracked and the 214 exhibited a visible haze. Adhesion was excellent in all cases.

3. WEATHER-O-METER (500 HOURS)

This is a cyclic standard exposure to artificially generated radiation and moisture, which simulate natural weathering parameters but cannot be directly compared to the weather conditions at any particular point on earth. Although the samples were stained to some extent by the aluminum foil masking used in the procedure, the No. 210 showed the least amount of haze increase.

4. UV EXPOSURE (36 DAYS)

The No. 210 formulation showed no appreciable haze change, while the No. 188 and No. 214 exhibited a steady increase.

5. CONSTANT HUMIDITY (10 DAYS)

The environment was further complicated by subjecting the specimens to both reciprocating arm and salt abraders. All three held up well to the reciprocating arm abrader for 3000 cycles with a very small change in haze level. The No. 210 formulation was the best by a small margin.

The salt abrasion, representing ice crystals, showed an almost immediate hazing of the No. 210 formulation to an exceptionally high value. The other two showed a less significant jump, but would have survived perhaps two exposures without exceeding a safe haze limit.

6. CYCLIC HUMIDITY EXPOSURE

Again, the three formulations survived 3000 cycles of the reciprocating arm without any appreciable change in haze. The salt abrasion was again the most severe of the two, with the No. 188 surviving 50 cycles before breaking through the coating and staying at an appreciably lower haze level than the other two.

7. SALT ABRASION CONTROL EXPOSURES

Without humidity exposure, all formulations remained within a marginally operable haze range not exceeding 9 percent. The No. 188 coating failed early, with the No. 214 following, and the No. 210 running to 250 cycles before breakthrough.

8. SOLVENT EXPOSURE

Again, haze measurements and salt abrasion were the principal means of analyzing the effect of solvent attack. Coated surfaces were first measured for haze and then abraded for 50 cycles (the 300 cycles originally specified destroyed the coating beyond obtaining useful data) and measured again for a control figure. Specimens were then exposed for 15 minutes to each of nine solvents. Haze measurements were then taken on the attacked area. The attacked area was subsequently subjected to 50 cycles of salt abrasion. All coatings fared well after the solvent attack, but the No. 210 appeared the least damaged after abrasion on an attacked surface.

9. COATING THICKNESS

The bulk of the data which utilized the salt impingement also indicated that coating thickness was a factor. Through the use of the scanning electron microscope, the coating thicknesses were measured as follows for the controlled exposures of paragraph 7:

No. 188	3.2 microns
No. 210	1.6 microns
No. 214	2.0 microns

10. DUCTILITY

The drop tests were too severe on the specimen size and thickness to provide any measure of energy required to crack the coating. These tests were abandoned. The mandrel test, however, was very revealing. Starting with the smallest diameter mandrel (11-in. radius), all three coatings were cold formed over the radius without the coating cracking. A smaller diameter mandrel of 5-1/2-in. radius was tried and the coatings did not crack, thereby exhibiting extreme ductility for our purposes.

11. THERMAL RESISTANCE

Use of a dry, reciprocating arm abrader was not successful at room temperature and was not expected to give any more reliable results at temperature extremes. The grid and backing tended to separate, ball-up, and gouge the specimen in an unpredictable manner. These tests were abandoned.

12. MECHANICAL TESTS

The flexural yield tests on controls and the three coating formulations showed little variation. The variances were predominantly on the positive side for tensiles and bearing strengths showing the coatings giving the overall composite an equal or greater strength.

The magnitude of variance is high. If tests were rerun, no decrease in the substrate strengths would be expected.

SECTION XI

COATING FORMULATIONS

The resulting formulations of the three coatings are shown in Table 27. The code No. 188 coating has no filler. The code No. 210 contains silicon dioxide particles, and code No. 214, aluminum dioxide.

TABLE 27. GOODYEAR AEROSPACE COATING FORMULATIONS IN PARTS BY WEIGHT

Components	Commercial designations	Coating codes		
		No. 188	No. 210	No. 214
Epoxy binder	XD-7080/DER 332 ①	7.5	7.5	7.5
Pre-hydrolyzed ethyl silicate	Silbond H-4 ②	5.7	5.7	5.7
Polysilicic acid	(Derived from TEOS)	25.1	25.1	25.1
Glacial acetic acid	-	29.4	29.4	29.4
Filler	Aluminum Oxid "C" ③ or EH-5 ④	-0-	21.0 (1.98 % EH-5)*	18.8 (2.5 % Aluminum Oxid "C")*
Water	-	29.4	8.4	10.6
Silane	A-187 ⑤	2.9	2.9	2.9
		100.0	100.0	100.0

Polysilicic acid preparation

Tetraethyl orthosilicate	83.7	Agitated until exotherm ceases
Hydrochloric acid (15%)	16.3	Allowed to stand 24 hours
	100.0	before compounding

Epoxy binder

XD-7080	71.4
DER 332	28.6
	100.0

① Dow Chemical Co.
② Stauffer Chemical Co.
③ DeGussa Inc.
④ Cabot Corp.
⑤ Union Carbide Corp.

*Water suspension, percentage by weight.
Notes:
1. Allow evaporation at room temperature for 1/2 hour.
2. Oven cure at +190 deg F for 16 hours for a stretched acrylic substrate.
3. Avoid skin and eye contact; use only with adequate ventilation.

SECTION XII

CONCLUSIONS

The coatings tested in Task II (119, 119/C, 120, and 130) could not be modified into hydrolytically stable, uncracked coatings.

Goodyear Aerospace tests indicate that "superhardness" is not the complete answer to a durable coating, and tradeoffs may be required.

Goodyear Aerospace No. 210 formulation ranks first in performance and is this company's choice as a reliable coating. The No. 188 coating appears less hard, and the No. 214 coating exhibits a haze problem which limits the amount of aluminum oxide which can be added.

The No. 210 coating is considered by Goodyear Aerospace to be flightworthy because of the previous performance during salt abrasion and its retention of properties after subjection to other environments not normally encountered by helicopter glazings.

From the standpoint of safety, the salt abrasion tests simulated haze that could be caused by ice particles. The test was originally designed to simulate a jet aircraft entry into an ice cloud. It appears that a relatively new coating could sustain such an exposure for at least a minute without exceeding an operable haze limit of 8 percent. A coating which has been exposed to 240 hours of extreme humidity-temperature cycling could possibly survive one short exposure and remain operable. Further testing would be required to make a quantitative comparison.

Currently, the No. 210 coating has only been applied and tested on stretched Plex 55. Extension of the formulation for use on as-cast acrylic will require either modification of the formulation or the development of a primer compatible with coating and substrate or both. The coating could be made slightly harder at the expense of some ductility.

Although outboard surface protection is more critical, better optical quality may be obtained by coating both sides of a glazing.

SECTION XIII

RECOMMENDATIONS

It is recommended that the current contract be modified to reinstate the originally planned, but subsequently deleted, full-scale flight test articles. These articles will be made and inspected in the production shop with the exception that engineering personnel shall supervise the coating of the formed blanks prior to final trim and assembly.

In addition, a program should be added which will extend the No. 210 coating to Plex II and polycarbonate through coating modification and/or the use of primers.

Further hardening of the No. 210 coating or optimizing for the best combination of properties should be considered.

The flight articles should be coated on both sides (if possible) on a formed stretched-Plex 55 substrate.

BIBLIOGRAPHY

1. Handbook of Surface Preparation, Snogren, Palmerton Publishing Co., Inc., 1974.

2. Paint Testing Manual, Gardner/Sward, 13th Edition, 1972, ASTM-STP 500.

3. A. Marks, Superhard Transparent Coatings, USAAMRDL-TR-75-22, Eustis Directorate, U.S. Army Air Mobility Research and Development Laboratory, Fort Eustis, Virginia 23604, April 1975, AD A010388.

4. Exploratory Development of Heat and Abrasion Resistant Coatings for Transparent Plastics, AFML-TR-76-115, Air Force Systems Command, July 1976.

5. "Synthetic Silicas, Important Pigments to the Paint Industry," William Georgov and Alexander A. Chasan, J.M. Huber Corp., Journal of Paint Technology, Vol. 43, No. 557, June 1971.

6. Abrasion Resistant Coating for Transparent Plastics, Loren Haluska and George Galic, Dow Corning Corp., 1976.

7. McCutcheon's Functional Materials, McCutcheon Division, MC Publishing Co., New Jersey, 1977 Annual.

8. McCutcheon's Detergents and Emulsifiers, North American Edition, McCutcheon Division, MC Publishing Co., New Jersey, 1977 Annual.

9. "Infrared Spectroscopy - Its Use in the Coatings Industry", Infrared Spectroscopy Committee of the Chicago Society for Paint Technology, Publisher: Federation of Societies for Paint Technology, Philadelphia, Pa., 1969.

10. TL 1078-OM-8111, Stereoscan 600 Scanning Electron Microscope Instruction Manual, Issue II, Vol. II, Morton Grove, Ill., Cambridge Instrument Co., Inc.

TEST RESULTS OF PVA BOUND COATINGS

TABLE A-1. TEST RESULTS OF PVA BOUND COATINGS

Panel no.	Substrate	Coating formulation	Coating application	Adhesion	Abrasion resistance	Remarks
SH-1	12 × 12 glass	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating good - no cracks
SH-2	12 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fractures during 212 deg F cure
SH-3	12 × 12 polycarbonate	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	10 percent removal	Light scratches	Coating developed fractures during 212 deg F cure
SH-4	12 × 12 acrylic	(No. 129C Modified) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA/DAA (10 percent)	Flow	No removal	Excellent	Coating developed fractures during 212 deg F cure
SH-5	12 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 133-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fish eyes upon drying. Coating also developed fractures during 212 deg F cure
SH-6	8 × 8 glass	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 50-acetic acid 53-PVA (10 percent)	Flow	No removal	Excellent	Coating appeared good except on coating edge. No cracks developed during 212 deg F cure
SH-7	8 × 8 glass	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 100-acetic acid 53-PVA (10 percent)	Flow	No removal	Excellent	Coating appeared hazy and developed rule lines. No cracks developed during 212 deg F cure
SH-8	6 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 113-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fish eyes upon drying. Coating also developed fractures during 212 deg F cure
SH-9	6 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 50-acetic acid 53-PVA (10 percent)	Flow	Trace removal	Excellent	Coating developed fractures during 212 deg F cure

TABLE A-1. TEST RESULTS OF PVA BOUND COATINGS (CONT)

Panel no.	Substrate	Coating formulation	Coating application	Adhesion	Abrasion resistance	Remarks
SH-10	12 × 12 acrylic	(No. 129C) 134-S_iO_2 (18.3 percent) 106-PVA (10 percent)	Spin Rpm-450 Time -15 s	No removal	Excellent	Film thickness approximately 20 microns. Radial flow lines apparent. Coating developed fractures during the 160 deg F cure
SH-11	12 × 12 acrylic	FA5 primer only	Flow	N/A	N/A	This panel was fabricated to determine if the primer might initiate the hard coat cracking. No fracturing of the primer coat occurred after exposure to 212 deg F cycle
SH-12	12 × 12 acrylic	(No. 129C modified) 63-S_iO_2 (18.3 percent) 20-H_2O 50-PVA/DAA (10 percent)	Spin Rpm-700 Time-15 s			No streaking or flow lines apparent in coating. Fractures developed in coating during 212 deg F cure. Film thickness approximately 7.6 microns.
SH-13	12 × 12 acrylic	(No. 129C modified) 63-S_iO_2 (18.3 percent) 15-H_2O 50-PVA/DAA (10 percent)	Spin Rpm-700 Time-20 s			Coating looked good. No streaking apparent. Fractures again developed during 212 deg F cure
SH-14	12 × 12 acrylic	(No. 129C) 63-S_iO_2 (18.3 percent) 15-H_2O 50-PVA (10 percent)	Spin Rpm-700 Time-20 s	No removal	Excellent	Coating appearance was good. Film fractures developed in all samples cured above 160 deg F
SH-15	12 × 12 acrylic	(No. 129C modified) 63-S_iO_2 (18.3 percent) 15-H_2O 50-25/5 PVA/DAA (10 percent)	Spin Rpm 700 Time-20 s	No removal	Excellent	Coating appearance was good. Film fractures developed in trace amounts in panels cured at 190 deg F and massive cracking occurred in samples cured at 210 deg F
SH-16	12 × 12 acrylic	(No. 129C) 63-S_iO_2 (18.3 percent) 15-H_2O 50-PVA (10 percent)	Spin Rpm-700 Time-20 s	Very poor	Excellent	Coating appearance was very poor. Radial flow lines and numerous inclusions were apparent
SH-17	12 × 12 acrylic	(No. 129C modified) 63-S_iO_2 (18.3 percent) 15-H_2O 50-25/5 PVA/DAA (10 percent)	Spin Rpm-700 Time-20 s	Very poor	Excellent	Coating appearance was very poor
SH-18	24 × 24 Plexiglas 55	(No. 129C modified) 63-S_iO_2 87-H_2O 25-25/5 PVA/DAA 25-Acetic acid	Flow	Very poor	Poor on top 25 percent of panel. Good to excellent on bottom 75 percent of panel.	Coating generally looked good. Minor film cracking initiating at the edges occurred during 175 deg F cure

APPENDIX A

TEST RESULTS OF PVA BOUND COATINGS

TABLE A-1. TEST RESULTS OF PVA BOUND COATINGS

Panel no.	Substrate	Coating formulation	Coating application	Adhesion	Abrasion resistance	Remarks
SH-1	12 × 12 glass	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating good – no cracks
SH-2	12 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fractures during 212 deg F cure
SH-3	12 × 12 polycarbonate	(No. 129C) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA (10 percent)	Flow	10 percent removal	Light scratches	Coating developed fractures during 212 deg F cure
SH-4	12 × 12 acrylic	(No. 129C Modified) 67-SiO_2 (18.3 percent) 83-H_2O 53-PVA/DAA (10 percent)	Flow	No removal	Excellent	Coating developed fractures during 212 deg F cure
SH-5	12 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 133-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fish eyes upon drying. Coating also developed fractures during 212 deg F cure
SH-6	8 × 8 glass	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 50-acetic acid 53-PVA (10 percent)	Flow	No removal	Excellent	Coating appeared good except on coating edge. No cracks developed during 212 deg F cure
SH-7	8 × 8 glass	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 100-acetic acid 53-PVA (10 percent)	Flow	No removal	Excellent	Coating appeared hazy and developed rule lines. No cracks developed during 212 deg F cure
SH-8	6 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 113-H_2O 53-PVA (10 percent)	Flow	No removal	Excellent	Coating developed fish eyes upon drying. Coating also developed fractures during 212 deg F cure
SH-9	6 × 12 acrylic	(No. 129C) 67-SiO_2 (18.3 percent) 33-H_2O 50-acetic acid 53-PVA (10 percent)	Flow	Trace removal	Excellent	Coating developed fractures during 212 deg F cure

Panel no.	Substrate	Coating formulation	Coating application	Adhesion[1]	Abrasion resistance[2]	Remarks
SH-19	8 × 8 soda-lime glass	(No. 130) 67.3-S_iO_2 83.0-H_2O 26.5-PVA 6.2-Alon gel	Flow	No removal	Excellent	Coating solution was very cloudy upon addition of Alon gel. The resulting coating was very coarse with a 3.9 percent haze content
SH-20	24 × 24 Plexiglas 55	(No. 129C) 126-S_iO_2 174-H_2O 100-PVA 50-Acetic acid	Flow	Very poor	Poor on top 30 percent; excellent on bottom 70 percent	Coating generally looked good. Typical inclusions apparent. Minor coating cracking occurred in the bottom one inch of panel. Coating thickness was approximately 10 microns
SH-21	8 × 8 soda-lime glass	(No. 130) 33.7-S_iO_2 41.5-H_2O 13.3-PVA 3.1-Alon gel	Flow	Excellent	Excellent	Coating solution was very cloudy. Resultant coating looked good. No cracking of the film occurred. Resultant haze was 0.5 percent
SH-22	8 × 8 Plexiglas 55	(No. 130) Same as SH-21	Flow	Trace removal	Good to excellent	Film coating was clear and contained typical inclusions. Film coating was badly cracked following 160 deg F cure. Resultant haze was 0.9 percent
SH-23A	8 × 8 Plex II	(No. 129C) 67-S_iO_2 83-H_2O 53-PVA	Flow	Excellent	Excellent	Primer - 1 percent Butvar B-72 in 1 PH. Cured coating was cracked. This was probably caused by the softness of the primer
SH-24A	12 × 12 Plex II	(No. 129C) 67-S_iO_2 20-H_2O 53-PVA	Spin Rpm-700 Time-20 s Primer and 129C coating	Excellent	Excellent	Cured panel was clear. Some radial flow lines apparent
SH-25A	8 × 8 Plex 55	(No. 119) 41-S_iO_2 49-H_2O 5-PVA 5-Alon gel	Flow	Trace removal	Excellent	Coating contained some fish eyes. Cured coating was cracked over the entire surface
SH-26A	8 × 8 Plex 55	(No. 120) 43-S_iO_2 52-H_2O 5-PVA 5-Alon gel	Flow	Excellent	Trace scratching	Coating had slight grainy appearance. Cured coating was cracked over the entire surface

NOTES:

1. Conducted using scribed tape test.

2. Conducted using 00 steel wool. "Excellent" indicates no scratches were produced.

TABLE A-2. MARKS SUPERHARD COATINGS PANEL IDENTIFICATION LOG

Panel no.	Substrate	Coating	Adhesion	Abrasion resistance	Remarks
Marks No. 1	0.250 Plex II	129C	No removal	Fair-good	Coating generally looks good. Minor small particles and typical dust inclusions. This coating has massive very light crazing and minor edge cracking.
Marks No. 2	0.090 Poly-carbonate	130	90 percent loss	Very poor	Coating contains several hazy streaks. Light film cracking extending approximately 1/2 inch in from edge. Normal dust and particle inclusions. No crazing noted.
Marks No. 3	0.090 Poly-carbonate	129C	70 percent loss	Poor	Coating looks OK. Typical inclusions. Minor edge cracks. No crazing noted.
Marks No. 4	0.187 Stretched Plex	130	No removal	Very poor	Coating looks good. Coating cracks extending approximately 4 inches in from one edge and 1/2 inch from other edges Minor flow lines were noted but no general crazing.
Marks No. 5	0.238 Plex II	130	Trace removal	Poor	Typical inclusions and edge cracks. Coating contains massive check marks approximately 3/16 inch long.

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TABLE A-3. MECHANICAL ABRASION OF GOODYEAR AEROSPACE APPLIED 129C COATING

Sample no.	Formulation	Reciprocating arm abrader percent haze versus number of cycles				Salt blast abrader Δ percent haze versus cycles		
		0	2000	4000	5000	0	30	200
SH-14-160	129C	0.5	0.3	0.5	0.5	0.8	0.0	0.0
SH-14-175	129C	0.4	0.5	0.5	0.5	-	-	-
SH-14-190	129C	0.5	0.5	0.6	0.6	-	-	-
SH-14-210	129C	0.5	0.5	0.9	1.3	0.3	0.0	0.0
SH-15-160	Modified 129C	0.4	0.4	0.4	0.5	0.2	0.0	0.0
SH-15-175	Modified 129C	0.4	0.4	0.4	0.5	-	-	-
SH-15-190	Modified 129C	0.5	0.4	0.4	0.5	-	-	-
SH-15-210	Modified 129C	0.4	(1-5.4)*	-	-	0.5	0.0	0.0

*It is felt that the sample failure was caused by the flaking away of the coating in the cracked areas, thus acting as an abrasive.

Substrates – Plex-55.

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TABLE A-4. MECHANICAL ABRASION OF MARKS APPLIED COATINGS

Panel no.	Substrate	Coating	Reciprocating arm abrader percent haze versus number of cycles				Salt blast abrader Δ percent haze versus cycles			
			0	500	1000	5000	0	30	100	200
Marks No. 1	0.250 Plex II	129C	0.2	0.2	0.4	0.4	0.0	-	0.2	0.7
Marks No. 2	0.090 Polycarbonate	130	1.2	1.7	32.5	D/C*	1.0	7.8	24.0	D/C
Marks No. 3	0.090 Polycarbonate	129C	1.2	1.2	1.2	0.9	2.0	-	5.6	D/C
Marks No. 4	0.187 Stretched Plex	130	0.9	19.2	D/C	-	0.8	-	1.2	0.8
Marks No. 5	0.238 Plex II	130	1.1	4.7	D/C	-	0.6	-	1.5	1.4

*Discontinued.

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TABLE A-5. HUMIDITY RESISTANCE OF 129C AND MODIFIED 129C COATINGS
(95-PERCENT RELATIVE HUMIDITY, 122° F; ONE 24-HOUR CYCLE)

Sample no.	Coating	Adhesion	Abrasion resistance	Film blisters
SH-14-160	129C	Poor	Good-fair	Numerous
SH-14-175	129C	Poor	Good-fair	Numerous
SH-14-190	129C	Poor	Good-fair	Numerous
SH-14-210	129C	Poor	Good-fair	Trace
SH-15-160	Modified 129C	Poor	Poor	Numerous
SH-15-175	Modified 129C	Poor	Poor	Numerous
SH-15-190	Modified 129C	Poor	Fair	Light
SH-15-210	Modified 129C	Poor	Good-fair	Trace

Substrates – Plex 55

TABLE A-6.   HUMIDITY RESISTANCE OF MARKS PANELS (AT 95-PERCENT
RELATIVE HUMIDITY AND 122° F)

Panel no.	Substrate	Coating	Results
Marks No. 1	Plex II	129C	Coating developed cracks prior to four 24-hour cycles. After eleven 24-hour cycles, no blisters had developed and coating remained clear.
Marks No. 2	Polycarbonate	130	Coating became opaque and developed cracks prior to one 24-hour cycle.
Marks No. 3	Polycarbonate	129C	Coating became opaque and developed cracks prior to one 24-hour cycle. Film blisters also developed in this sample.
Marks No. 4	Stretched Plex	130	Coating developed cracks prior to four 24-hour cycles. After eleven 24-hour cycles, no blisters had developed and coating remained clear.
Marks No. 5	Plex II	130	Coating developed cracks prior to four 24-hour cycles. After eleven 24-hour cycles, no blisters had developed and coating remained clear.

FILLER PROCESSING REACTIONS

TABLE B-1. FILLER PROCESSING REACTIONS

Material (16)	Average particle size, μ	Susceptibility (15) Acid	Neutral	Base	Centrifuging 5 min at 6000 RPM	10 min at 18,000 RPM	pH [1]	Form	Type	Remarks
ALON (2)	0.03	Susp	Susp	Ppt	Ppt and Susp	Gel and Ppt	4.55 M	Gamma Agglomerates	Al_2O_3	No longer manufactured
Aluminum Oxid "C" (14)	0.02	Susp	Susp	Ppt	Ppt and Susp	Gel and Susp		Gamma Agglomerates	Al_2O_3	Fumed
ATTAGEL-50 (3)	0.14	Visc. Floc	Susp	Susp	All Ppd	-	9.0 M	Crystalline needles	Complex silicate	Basically $Mg_5(Si_8O_{20})$· $4 H_2O$ and $Al_6(Si_2O_{13})$
Linde 100 percent Gamma (4)	0.05	Susp	Ppt	Ppt	Ppt and Susp	Clear tan gel	7.0 M	Cubic crystals	Al_2O_3	Calcined Alum
Linde 0.05 polishing pwdr	0.05	Susp	Susp	Ppt	All Ppd	-	6.9 M	Cubic crystals	Al_2O_3	Calcined Alum
Hydral 710 (11)	1.00	Ppt	Ppt	Susp	-	-	8.1 M	Amorphous	Al_2O_3	Hydrated Alumina - settled prior to centrifuging
Hydral 710-SD	1.00	Ppt	Susp	Susp and Ppt	Lgt Susp	-	8.1 M	Amorphous	Al_2O_3	Hydrated spray dried - insufficient fine particles in suspension
Supergrn A-16 (11)	>1.00	Lgt Susp	Lgt Susp	Lgt Susp	1	-	-	Amorphous	Al_2O_3	Calcined Alumina - settled prior to centrifuging
GHA-731 (12)	>1.00	Susp	Ppt	Ppt	All Ppd	-	7.9 M	Amorphous	Al_2O_3	Hydrated Alumina
Microfil (12)	>1.00	Ppt	Ppt	Ppt	All Ppd	-	7.4 M	Amorphous	Al_2O_3	Hydrated Alumina
QUSO G-32 (5)	1.00	Ppt	Susp and Ppt	Susp and Ppt	Hvy Ppt Lgt Susp	Clear tan gel	8.4 M	Structured particles	SiO_2	Hydrophillic precipitated agglomerates
QUSO XN	0.015	Ppt	Susp and Ppt	Susp and Ppt	Hvy Ppt Lgt Susp	Clear tan gel	7.6 M	Structured particles	SiO_2	Filler material
DMSIL A-108 (6)	1.12	Ppt	Susp and Ppt	Susp and Ppt	All Ppt	-	6.9 M	Amorphous powder	SiO_2	Some Ppt could be shaken back into suspension
NALCO 2327 (7)	0.02	Cloudy increase	Sigtly cloudy	Sligtly cloudy	Nothing Ppd	Lg quantity opalescent gel and susp	9.2 L	Water suspension	SiO_2	Treated NH_4OH 40 percent solids
NALCOAG 1034A (7)	0.016-0.022	Cloudy increase	Sligtly cloudy	Gel	Sigt gel and suspension	Small clear gel and susp	3.1 L	Water suspension	SiO_2	Acidified 34 percent solids
NALCOAG 1129	0.016-0.025	Cloudy increase	Sligtly cloudy	Gel	Nothing Ppd	Very small clear gel and susp	3.5 L	Water-alcohol suspension	SiO_2	Sensitive to salts and anionic surfactants 30 percent solids

TABLE B-1. FILLER PROCESSING REACTIONS (CONT)

Material	Average particle size, μ	Susceptibility			Centrifuging		pH (1)	Form	Type	Remarks
		Acid	Neutral	Base	5 min at 6000 RPM	10 min at 18,000 RPM				
NALCOAG 1130	0.008	Gel	Lgt Susp	Lgt Susp	Nothing Pptd	Small very clear gel	10.0 L	Water suspension	SiO$_2$	30 percent solids
NALCOAG 1160	0.040-0.060	Susp	Ppt	Ppt			8.5 L	Water suspension	SiO$_2$	50 percent solids
NOVACITE L-337 (8)	3 percent <1.00	Ppt	Ppt	Ppt	All Pptd	-	7.6 M	Crystalline platelets	SiO$_2$	Some Ppt could be shaken back into suspension
LUDOX AM (9)	0.012	Ppt	Susp	Susp	Susp	Med. clear gel	8.9 L	Water suspension	SiO$_2$	Treated with sodium hydroxide Neg charge Surface modified with aluminate
LUDOX LS	0.012	Susp	Susp	Susp	Susp	Med. clear gel	8.2 L	Water suspension	SiO$_2$	Treated with sodium hydroxide Neg charge
CAB-O-SIL M-5 (2)	0.014	Susp	Susp	Susp	Semi-clear gel	Lg opalescent gel	3.5 to 4.2 L	Amorphous agglomerates	SiO$_2$	Fumed
CAB-O-SIL EH-5	0.007	Susp	Susp	Susp	Semi-clear gel	Lg opalescent gel	3.5 to 4.2 L	Amorphous agglomerates	SiO$_2$	Fumed
SILCRON G-640 (10)	4.0	Ppt	Susp	Ppt	Lgt susp; some gel	Med. opalescent gel	4.0 L	Gel particles	SiO$_2$	
ZOPAQUE RCL-6 (10)	-	Ppt	Ppt	Ppt	-	-	6.5-7.5L	Paint pigment	TiO$_2$	Settled out prior to centrifuging
Imperial X-1861 (13)	-	Ppt	Susp and Ppt	Ppt	Lgt suspension	-	7.2 M	Paint pigment	Cr$_2$O$_3$	Insufficient solids
Silicon Carbide	7.0-9.0	Ppt	Sus	Ppt	Sgt Susp Hvy Ppt	All Ppt	7.0 M	Blocky shaped particles	SiC	

Notes:

1. L = from literature   M = measured
2. T.M. Cabot Corp., Boston, MA
3. T.M. Englehard Minerals & Chemicals Corp., Attapulgus, GA
4. T.M. Union Carbide Corp, San Diego, CA
5. T.M. Philadelphia Quartz Co., Philadelphia, PA
6. T.M. Illinois Minerals Co., Cairo, ILL
7. T.M. NALCO Chemical Co., Chicago, ILL
8. T.M. Malvern Minerals Co., Hot Springs National Park, ARK
9. T.M. E I duPont de Nemours & Co. (INC.), Wilmington, DEL
10. T.M. SCM Corp., Baltimore, MD
11. T.M. Aluminum Company of America, Pittsburgh, PA
12. T.M. Great Lakes Foundry Sand Co., Troy, MI
13. T.M. Hercules, Inc., Wilmington, DEL
14. T.M. Degussa Inc., Teterboro, N.J.
15. Susceptibility test was performed by adding 2 drops of 4N-HCl to 10 ml of suspension or 2 drops of 1N-NaOH to 10 ml of suspension
16. All solid fillers were sheared in a 2 percent solids/water suspension at top Waring blender speed for 5 minutes prior to centrifuging.

APPENDIX C

RATE OF SOLVENT EVAPORATION

1. INTRODUCTION

The following study was carried out to determine the rate of solvent evaporation from superhard coatings and certain raw materials.

Solvent evaporation controls the setting time of most coatings. The solvent must remain in the coating long enough to allow flow sufficient to produce adequate adhesion, gloss, and leveling. It must evaporate fast enough to prevent sagging and inadequate film thickness.

The relationship between evaporation rate and solvency is always critical with blends of different solvent types. Such is the case for superhard coating formulations. Besides the organic solvents present there are also present in the composition water and acetic acid, which should also be taken into consideration. Solvents rarely evaporate at the same rate; therefore, the composition and resulting solvency change as the blend evaporates. Film properties can vary widely because of this phenomenon. Retained solvent can affect coating properties such as clarity, gloss, adhesion, water resistance, and hardness.

If the solvent evaporation rate of several different formulations were known, it would facilitate further modification of these compounds. The data could also be used in cure cycle recommendations.

2. TEST METHOD

Solvent evaporation rate is not an absolute value in practical situations because it depends upon environmental conditions. Temperature, air movement, the presence of a solute, surface area, and humidity are factors that affect the evaporation of a single solvent.

The following test method was found to give reproducible results. In all cases available equipment was used.

Step 1: Foil-backed blotters were cut from Whatman® No. 54 filter paper and standard aluminum foil so that the resulting blotter assembly would fit the balance pan of a Type H6T Mettler® balance.

Step 2: The foil-backed blotter assembly was placed on the balance pan and weighed. Then, with the use of a hypodermic needle, approximately 2 cc of a liquid in question were applied onto the blotter and immediately weighed to determine the initial amount of liquid added.

Step 3: With both doors of the balance left open, and with the balance left on "full release", periodic readings were taken.

Step 4: Data was recorded on a form which listed: Δ time, time, weight, Δ weight, and percent Δ weight. Readings were usually taken every 5 minutes for a period of not less than 90 minutes (see Figure C-1).

Step 5: Values collected were then translated into data which was plotted on graph paper as percent weight loss versus time.
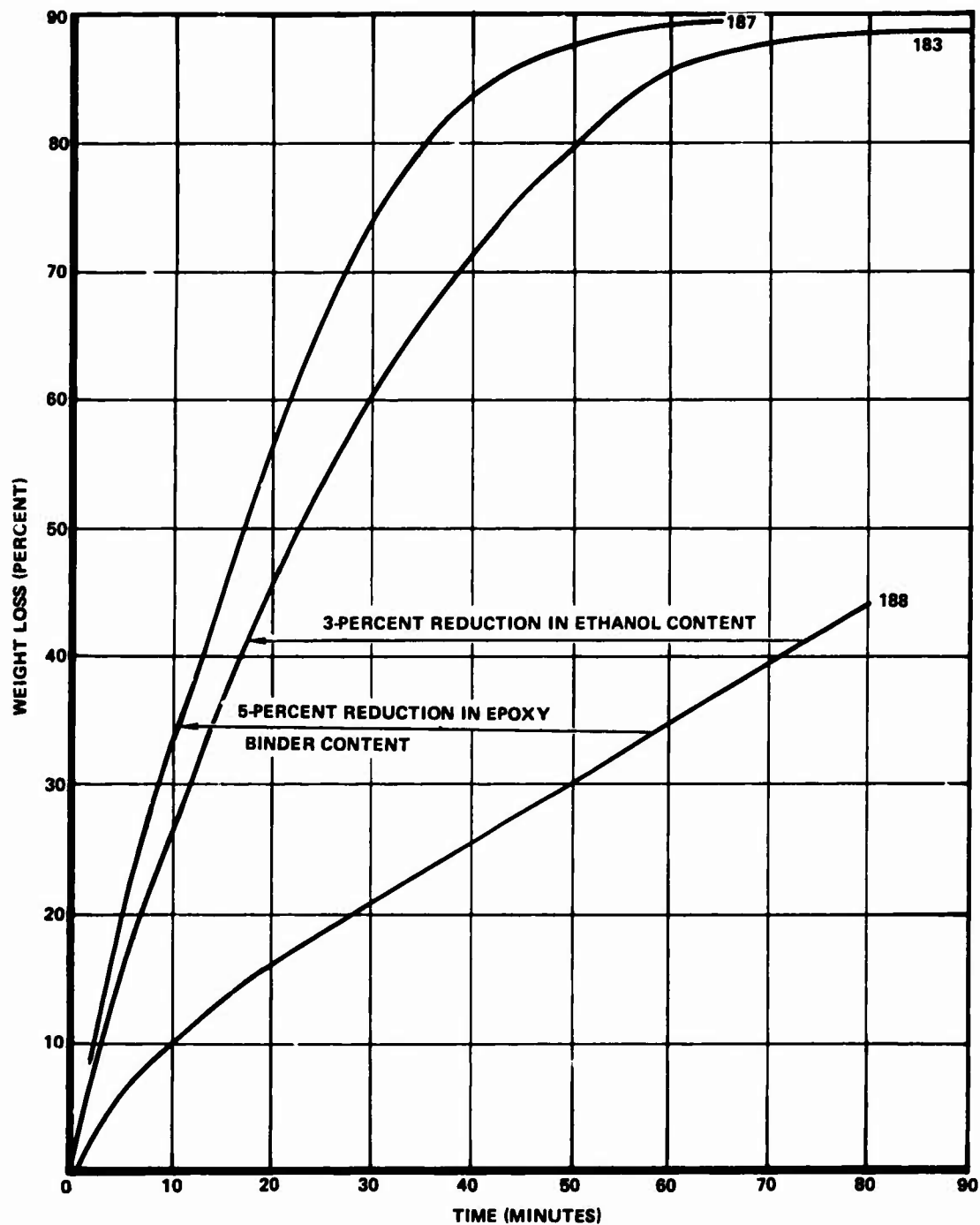

Figure C-1. Typical Evaporation Curves of Three Ratioed Mixes of the Same Constituents

APPENDIX D

EQUIPMENT

1. GENERAL

This program required a variety of equipment to aid in the compounding of the various superhard coatings, the application of the coatings to various plastic substrates, and the evaluation of the durability of the cured coating following exposure to different test conditions.

2. DISPERSER

Large quantities of filler particles are dispersed and freed from clusters and agglomerates. To this end a Gaulin Model 15M Sub-Micron Disperser was used (see Figure D-1). The disperser has a circulating capacity of 15 gallons per hour and is operated at 9500 psi to achieve the desired particle dispersion. For smaller quantities a Waring blender was used.

3. CENTRIFUGE

A Sorvall SS-3 Automatic Superspeed centrifuge (see Figure D-2) was used to separate the larger particles and agglomerates from a suspension. Heavy opaque particles of the dispersion were removed at 9000 rpm. The lighter, more translucent fractions of the dispersion remained in suspension.

4. GOODYEAR AEROSPACE RECIPROCATING ARM ABRADER

The Goodyear Aerospace reciprocating arm abrader, Part No. A71QS337 (see Figure D-3), has been used extensively in evaluating the abrasion resistance of both monolithic and coated transparent glazing materials. The device also has been incorporated in the proposed Aerospace Material Specification AMS 3614, Polycarbonate Sheet and Parts, Optical Grade, Coated, by the Society of Automotive Engineers.

5. GOODYEAR AEROSPACE SALT BLAST ABRADER

The salt blast abrader (see Figure D-4) attempts to simulate flight conditions through clouds of ice particles by impacting the test sample with successive 1/2 second blasts of minute salt particles. The resulting abraded area is a circle 1 inch in diameter. The increase in haze is used as a measure of the abrasion resistance.
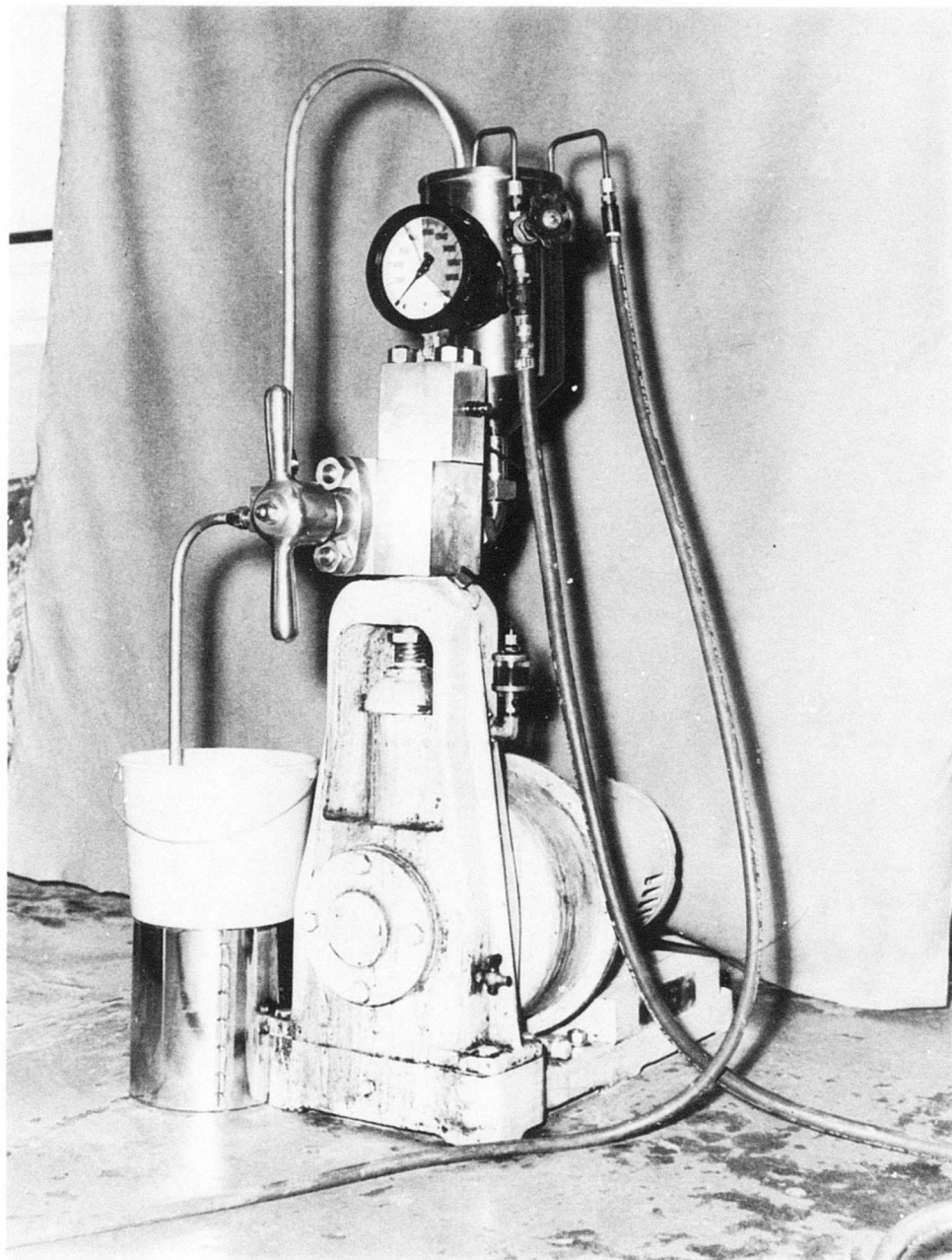
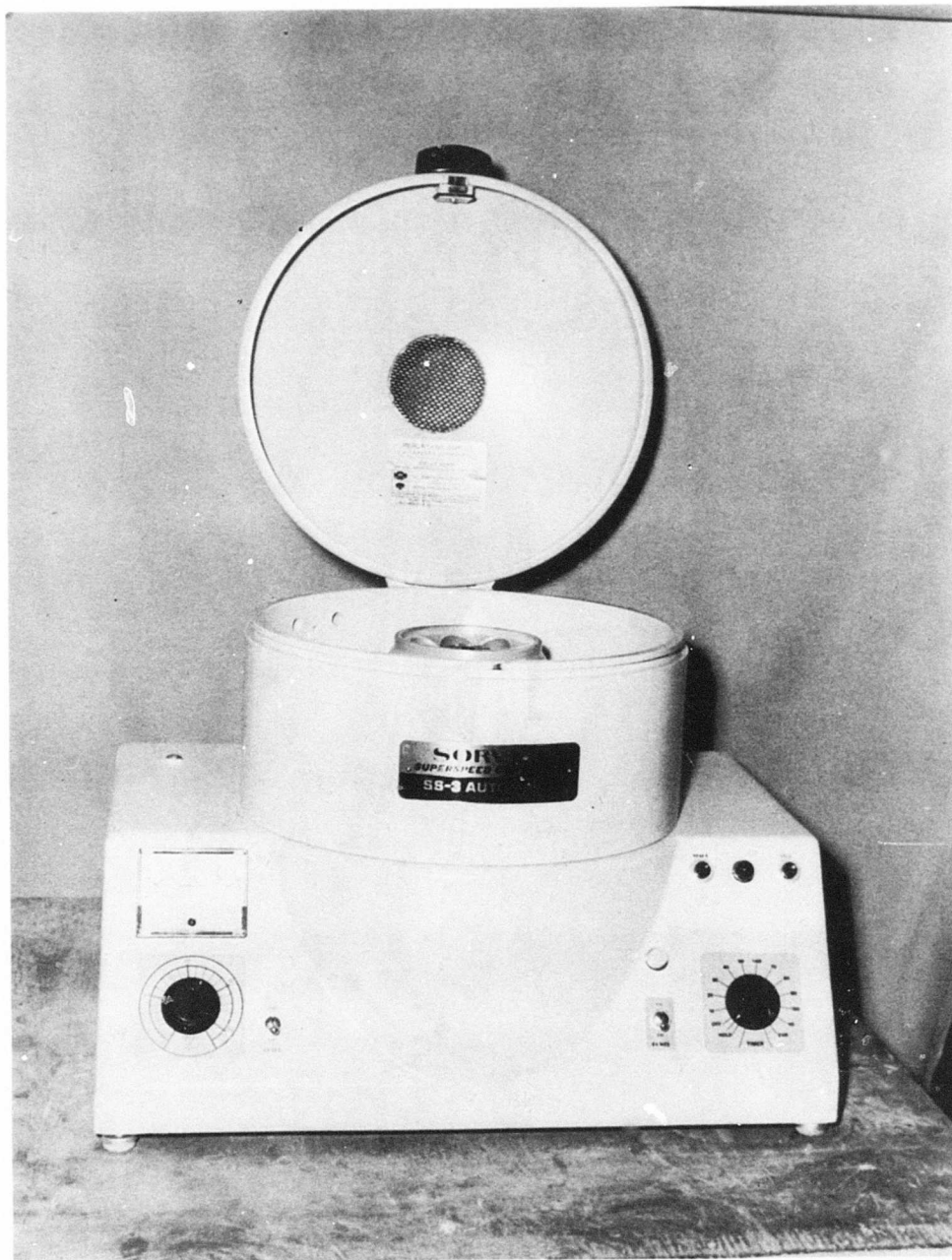Figure D-1.   Gaulin Sub-Micron Disperser
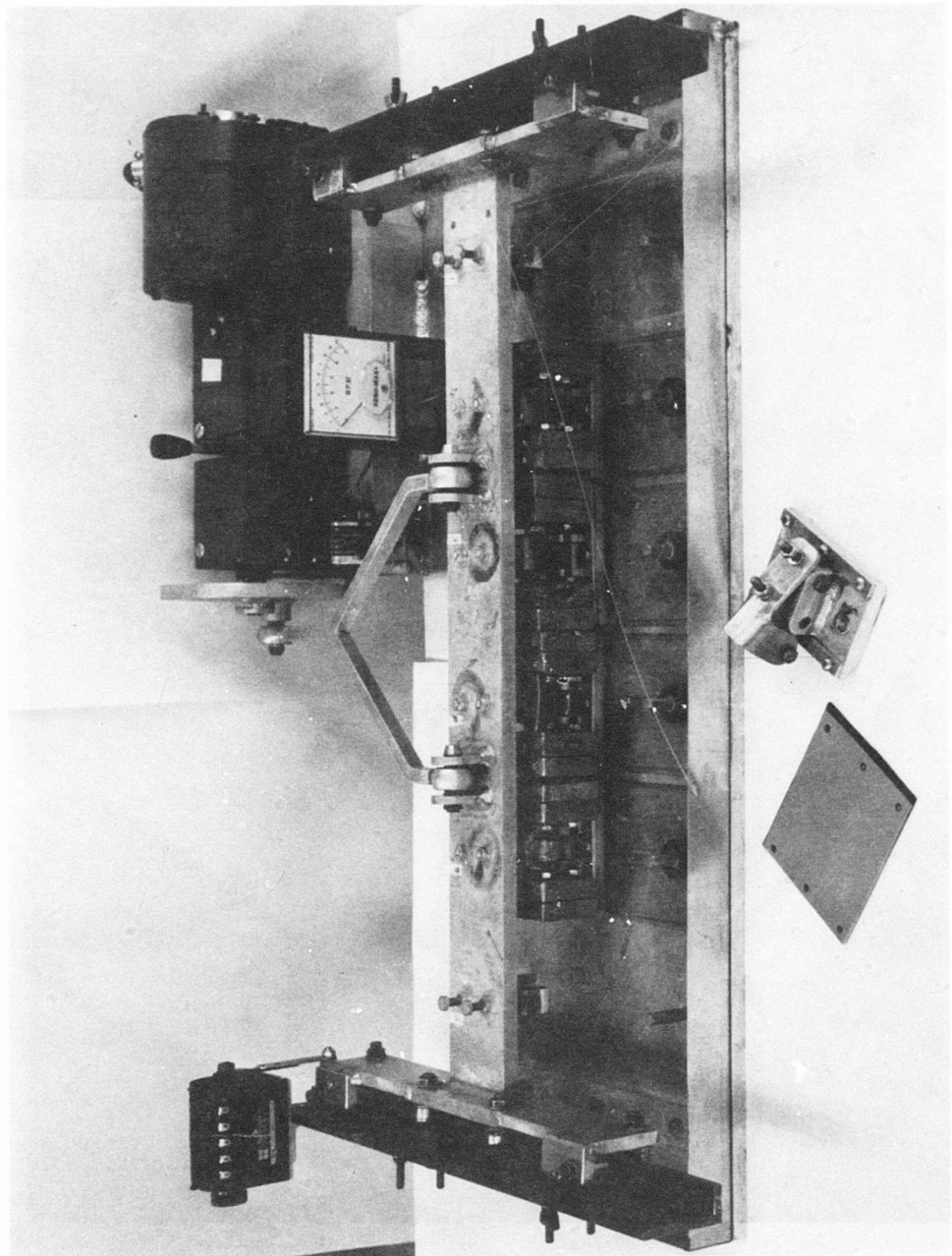
Figure D-2. Sorvall SS-3 Centrifuge

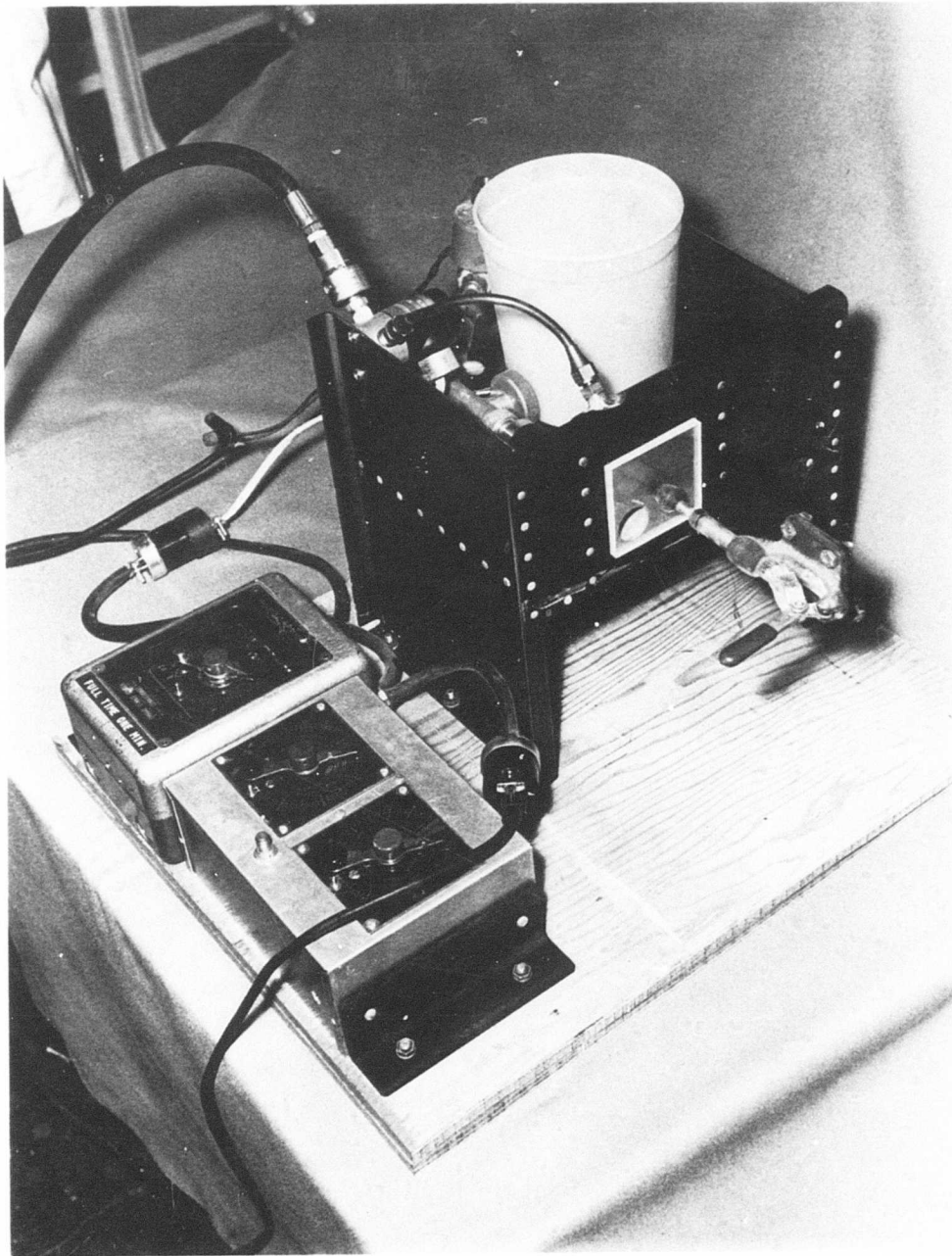Figure D-3. Goodyear Aerospace Reciprocating Arm Abrader

Figure D-4. Goodyear Aerospace Salt Blast Abrader

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6. SCANNING ELECTRON MICROSCOPE

This instrument has been found to be the most direct way of measuring film thickness. A target specimen approximately 1/2 in. on a side is cut from the coated substrate. This is cemented to a holder and sputtered with aluminum to prevent static discharge. The image is focused on a CRT screen and the edge striation between coating and substrate located. One or several pictures may be taken which automatically records a bar whose length is identified in microns. Through the use of this scale and the specimen angle which can be recorded, the actual film thickness can be calculated. See Figure D-5 for a photograph of the Stereoscan 600 scanning electron microscope. [2]

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[2] Techniques for operating the Stereoscan 600 can be found in Cambridge Instrument Co. publication TL 1078-OM-8111, Stereoscan 600 Scanning Electron Microscope Instruction Manual, Issue II, Vol. II, Morton Grove, Ill., Cambridge Instrument Co., Inc.
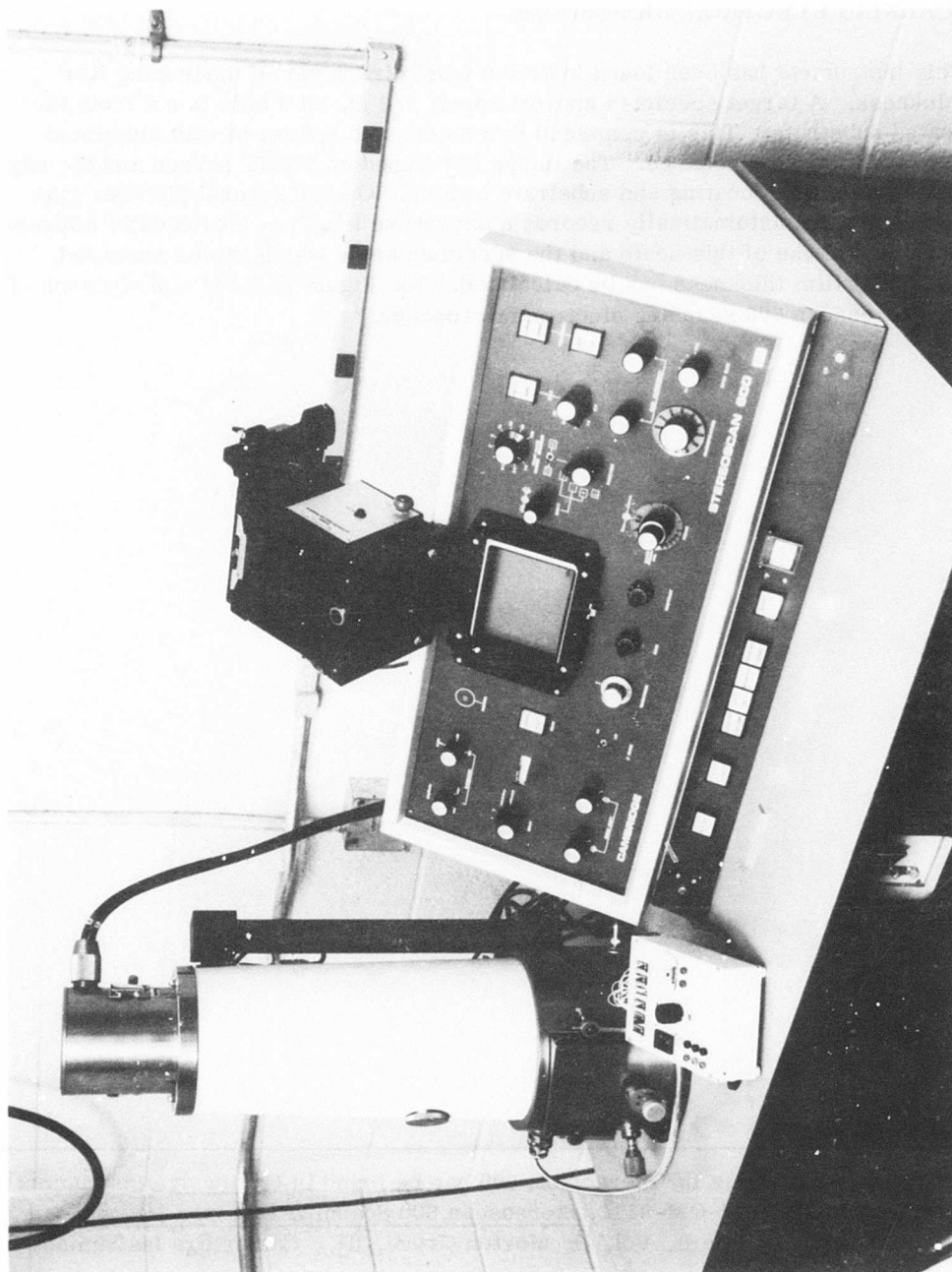
Figure D-5. Scanning Electron Microscope (Stereoscan 600)

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